Quantum electrodynamical study of bimolecular scattering effects in Raman spectroscopy

D. L. Andrews and N. P. Blake

School of Chemical Sciences, University of East Anglia, Norwich NA4 7TJ, United Kingdom
(Received 28 March 1989; revised manuscript received 4 December 1989)

In this paper a quantum electrodynamical theory of cooperative Raman scattering in fluids is developed. The process is one in which pairs of molecules undergo concerted Raman transitions via an intermolecular energy transfer mechanism. The formalism is also extended to chromophore pairs in which intramolecular energy transfer is involved. Using the Power-Zienau-Woolley multipolar Hamiltonian, intensity equations of the Kramers-Heisenberg type are derived which are valid over all regions of molecular separation. In the near zone it is illustrated how the intensity of cooperative scattering is simply that obtained by consideration of the instantaneous response of one molecule to the scalar field generated by another. Within this regime it is shown that the rate of scattering has the familiar R^{-6} dependence on intermolecular separation R associated with interacting induced dipoles. In the far zone it is demonstrated that the fully retarded and causal interaction between molecules is mediated through virtual photon coupling, and that this leads to a result for the intensity that dies off with R^{-2}. This long-range-interaction contribution to the overall scattering intensity is generally ignored in collisional treatments of intermolecular interactions, yet is likely to be of more significance than higher-order multipole terms in near-zone calculations. Finally it is shown how bands in a Raman spectrum due to cooperative scattering effects may be identified by their unique pressure characteristics, or by observation of light scattering that occurs outside the interaction volume of the laser beam. In the case where the scattering occurs between molecules or chromophores held in a fixed orientation with respect to one another, it is demonstrated how detection may be facilitated through the manifestation of a differential scattering effect.

I. INTRODUCTION

It is well known that the environment of a molecule can affect its optical scattering characteristics. The presence of solvents with high refractive index, for example, can lead to local field enhancements and hence intensity increases. Such solvent effects, which can occur even at moderate densities, are known to lead to solvatochromic effects and are often associated with changes in vibrational frequencies of the solute. Such modifications to the solute spectrum are generally pressure dependent, indicating that they arise as a result of molecular proximity effects.

One such mechanism by which these effects are mediated is the dipole-induced-dipole[1-4] (DID) mechanism, in which the interaction potential has the familiar R^{-6} dependence on molecular separation.[5] The extreme distance sensitivity of this mechanism is such that phenomena in which it is implicated are normally referred to as collisional. In fact, most DID calculations are based on nonrelativistic treatments which fail to give a result general for all regions of molecular separation. This occurs because of the assumption that the response of one molecule to the presence of another is mediated through the instantaneous coupling of the neighboring molecule's electrostatic scalar potential (see, for example, Ref. 6). This approach produces results which are, therefore, only valid in regions where relativistic contributions are negligible (the near zone).[7]

More rigorous relativistic quantum electrodynamical treatments, which consider the interaction of neighboring molecules as being mediated by virtual photon coupling, show that the interaction potential at large separations (the far zone) in fact dies off as R^{-2}, reflecting the classical limit for radiative energy transfer. Consequently, significant coupling effects persist even in the absence of collision in this region. Craig and Thirunamachandran[8] have derived equations for the Maxwell field in the vicinity of a molecule by consideration of how the vector potential is modified in relation to the field *in vacuo*. In their treatment, conducted within the Heisenberg representation, the molecule plays a passive role via its polarizability. The resultant modifications to the vacuum field are manifest in nonunity refractive indices[9] and other related local field effects. However, no net energy is transferred in the associated scattering processes.

A spectroscopically more interesting process is one in which molecules of the ensemble interact inelastically with the radiation field. Here bimolecular effects are especially pronounced in connection with inner coordination shells, hydrogen-bonded species and van der Waals complexes. In each case the interaction between molecules can lead to modifications in the polarization properties of the scattered light, Raman frequency shifts, and changes in the pressure characteristics of Raman bands.[10-13] Multiple scattering processes can also lead to other interesting features in a Raman spectrum. For example, the interaction between two centers can provide a mechanism for energy exchange such that the process

$$A + B + \hbar\omega \rightarrow A^* + B^* + \hbar\omega' \qquad (1.1)$$

occurs, leading to the possibility of observing bimolecular combination bands in regions where neither A nor B shows normal Raman activity, i.e.,

$$\hbar(\omega - \omega') = (E_{\alpha'\alpha} + E_{\beta'\beta}) , \qquad (1.2)$$

$$\hbar(\omega - \omega') \neq E_{\alpha'\alpha}, E_{\beta'\beta} , \qquad (1.3)$$

where the Raman transition at A is designated $|\alpha'\rangle \leftarrow |\alpha\rangle$, and that at B is $|\beta'\rangle \leftarrow |\beta\rangle$.

This type of synergistic Raman scattering may also occur as a result of coupling between chromophores in the *same* molecule. Here the operation of an *intra*molecular scattering mechanism leads to the appearance of combination bands due to excitation of two normal modes within the molecule. This effect is more commonly viewed as an induced anharmonicity in the group vibrations originating from the interaction between transition dipoles in the two chromophores. As we shall see, chromophore coupling can lead to an induced chirality manifest in the appearance of circular differential scattering (even in the electric dipole approximation), an effect especially pronounced in Raman 90° scattering experiments. This mechanism is sensitive both to the separation distance and the relative orientation of the two interacting chromophores. It is, therefore, apparent that a good understanding of this effect in normal scattering experiments could lead to information about the chemical environment of the scattering sites.

II. THEORY

Within the framework of quantum electrodynamics (QED) the effect of interacting molecules or chromophores can be described in terms of virtual photon coupling, such that the interactions which occur between charges in different molecules propagate with the speed of light. In this case it is therefore necessary to ensure that all molecular interactions are fully retarded, taking account of the finite speed of propagation. In this treatment we utilize the multipolar Hamiltonian of Power and co-workers.[14,15] This form of interaction Hamiltonian contains no static term and is manifestly causal. In this sense it has a distinct advantage over the minimal coupling formalism as derived in the Coulomb gauge, which describes radiation-molecule interactions in terms of the scalar potential φ and the transverse vector potential $\mathbf{a}^{\perp}$. In this representation both φ and $\mathbf{a}^{\perp}$ are nonlocal and not fully retarded.[16] Hence the interaction Hamiltonian includes static contributions which give rise to a false instantaneous precursor signal. In any complete calculation the static signal, which arises from terms involving $\mathbf{a}^{\perp}$, exactly cancels the longitudinal electrostatic interaction, giving a Lorentz-covariant result. Of course, either choice of Hamiltonian gives the same result;[14,17-25] however, by adopting the multipolar Hamiltonian it is possible to ensure causality from the outset greatly simplifying subsequent calculations.

Assuming that the radiation wavelength is long in comparison to the molecular dimensions of the site at which the radiation interaction occurs, it is valid to retain the leading, electric dipole, term in the multipolar

expansion. In the Heisenberg representation the interaction Hamiltonian has the explicit form

$$H_{\text{int}}^{\xi}(\mathbf{k}, \lambda, t) = -\epsilon_0^{-1} \boldsymbol{\mu}(\xi, t) \cdot \mathbf{d}^{\perp}(\mathbf{k}, \lambda, \mathbf{R}_{\xi}, t) , \qquad (2.1)$$

where $\boldsymbol{\mu}(\xi)$ is the electric dipole moment operator for a molecule ξ at a position $\mathbf{R}_{\xi}$, ϵ_0 is the vacuum permittivity, and $\mathbf{d}^{\perp}$ is the transverse electric displacement operator which for the mode with propagation vector $\mathbf{k}$ (circular frequency $\omega = c|\mathbf{k}|$) and polarization λ, is given by

$$\mathbf{d}^{\perp}(\mathbf{k}, \lambda, \mathbf{r}, t) = i(\hbar c k \epsilon_0 / 2V)^{1/2}$$

$$\times \{ e^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}, t) e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$- \bar{e}^{(\lambda)}(\mathbf{k}) [a^{(\lambda)}(\mathbf{k}, t)]^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{r}} \} , \qquad (2.2)$$

where $\mathbf{e}^{(\lambda)}$ is a polarization vector in the direction of the electric field, $a^{(\lambda)}(\mathbf{k}, t)$ and $[a^{(\lambda)}(\mathbf{k}, t)]^{\dagger}$ are the normal photon annihilation and creation operators, respectively, and where for a plane wave description of the radiation field we have $a^{(\lambda)}(\mathbf{k}, t) = a^{(\lambda)}(\mathbf{k}) \exp -i\omega t$.

In this paper we define the incident laser beam in terms of its polarization vector $\mathbf{e}^{(\lambda)}(\mathbf{k})$, and the scattered light by the polarization vector $\mathbf{e}'^{(\lambda)}(\mathbf{k}')$. Within the Power-Zienau-Woolley formalism of quantum electrodynamics,[14,15] all molecular interactions are mediated by the exchange of virtual photons, which we here designate by wave vector $\mathbf{p}$ and polarization label ε. By assuming that all interactions between molecules occur *outside* the region of wave-function overlap, it is possible to define the initial and final states of the cooperative scattering process described in Eqs. (1.1)–(1.3) as

$$|i\rangle = |\alpha; \beta; n; 0; 0\rangle , \qquad (2.3)$$

$$|f\rangle = |\alpha'; \beta'; (n-1); 1; 0\rangle , \qquad (2.4)$$

where the sequence in the ket denotes, respectively, the molecular state of A; molecular state of B; occupation number of the laser beam in the direction of propagation $\mathbf{k}$; occupation number of the scattered photon mode in the direction of scattering $\mathbf{k}'$; occupation number of the virtual photon states, $(\mathbf{p}, \varepsilon)$.

In principle there are two allowed cases, corresponding to where either (a) one center absorbs the laser photon and the scattered photon emerges from the other center, or (b) both the absorption and emission occur at the same center. In each case the virtual photon essentially propagates the energy mismatch between the two centers. These two cases, which are illustrated in Fig. 1, are associated with quite different selection rules since the former mechanism involves an even number of photon interactions at each center, and the latter an odd number. In fact, case (a) results in the normal Raman selection rules for the transitions at each center, while case (b) is associated with hyper-Raman selection rules at one center and infrared selection rules at the other. In this paper we concentrate on the case where the transitions at both A and B satisfy the normal Raman selection rules, and we therefore restrict our attention to mechanism (a).

The rate of cooperative scattering can be calculated via the fourth-order perturbation term in the Dyson equation, so that the evolution operator $U(t, 0)$ for the process is given as[26]
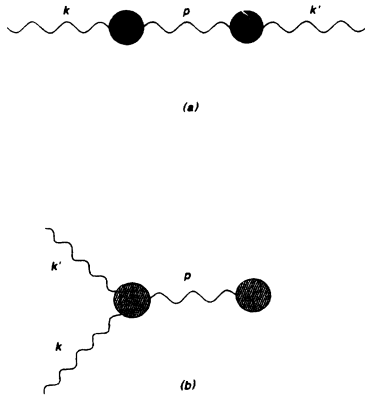
FIG. 1. Two possible bimolecular scattering mechanisms; (a) corresponds to cooperative Raman scattering and (b) distributive Raman scattering.

FIG. 2. Two collapsed time-ordered diagrams for a scattering event involving the annihilation of a laser photon at A and creation of a scattered photon at B.

$$U(t,0)=\frac{(i\hbar)^{-4}}{4!}T\left[\int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \int_0^t dt_4 H_{\text{int}}^A(\mathbf{k},t_1)H_{\text{int}}^A(\mathbf{p},t_2)H_{\text{int}}^B(\mathbf{p},t_3)H_{\text{int}}^B(\mathbf{k}',t_4)\right] ,\qquad (2.5)$$

where T is the Dyson time-ordering operator. Here there is implicit summation over virtual-photon modes, and polarization labels are dropped for brevity. The amplitude of the probability for finding the system in a state $|f\rangle$ at time t due to the interaction switched on at $t=0$, given that at time zero the state was in a state $|i\rangle$, is given by $c_{fi}(t)$,

$$c_{fi}(t)=\langle f|U(t,0)|i\rangle , \qquad (2.6)$$

where $|f\rangle$ and $|i\rangle$ are given in Eqs. (2.2) and (2.3). To calculate the result for $c_{fi}(t)$ explicitly requires the summing of all time orderings in Eq. (2.5). This calculation is facilitated by the use of time-ordered diagrams, and Fig. 2 illustrates four typical contributions.

For the case where molecular centers A and B are identical one needs to sum a total of 48 contributions allowing for absorption of $\mathbf{e}^{(\lambda)}(\mathbf{k})$ at A and scattering of $\mathbf{e}'^{(\lambda)}(\mathbf{k}')$ at B, or vice versa. However, in what follows we demonstrate how the cooperative scattering process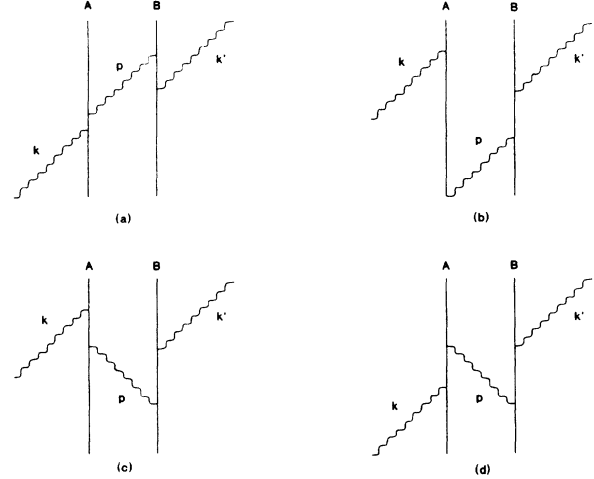 may be described in terms of the collapsed time-ordered diagrams given in Fig. 3. In this form we obtain an interesting physical insight into this pairwise interaction, and its relation to multiple-scattering processes.

To establish the equivalence of the two sets of time-ordered diagrams we define a canonical transformation such that interactions of lowest order are eliminated from the calculation.[27] In this way it is possible to define two effective interaction Hamiltonians which describe the nature of the scattering process at the two molecular sites. We start by defining the Hamiltonian H, which, for the cooperative scattering process, may be written as

$$H=H_0+H_{\text{int}}^A(\mathbf{p},\epsilon)+H_{\text{int}}^B(\mathbf{p},\epsilon)+H_{\text{int}}^A(\mathbf{k},\lambda)+H_{\text{int}}^B(\mathbf{k}',\lambda') , \qquad (2.7)$$

where H_0 represents the Hamiltonian of the uncoupled molecule-radiation system, and subsequent terms denote coupling perturbations. By methods described in detail elsewhere,[27,28] it can be proven that this Hamiltonian is just one of a set of Hamiltonians of the form

$$H=H_0+H_{\text{int}}^A(\mathbf{p},\epsilon)+H_{\text{int}}^B(\mathbf{p},\epsilon)+H_{\text{int}}^A(\mathbf{k},\lambda)+H_{\text{int}}^B(\mathbf{k},\lambda')$$

$$-i\{[S,H_0]+[S,H_{\text{int}}^A(\mathbf{p},\epsilon)]+[S,H_{\text{int}}^B(\mathbf{p},\epsilon)]+[S,H_{\text{int}}^A(\mathbf{k},\lambda)]+[S,H_{\text{int}}^B(\mathbf{k},\lambda')]\}-\tfrac{1}{2}[S,[S,H_0]]+\cdots \} , \qquad (2.8)$$

whose Lagrangians all give rise to the same Heisenberg equations of motion. Here S is termed the generator, and may have any form whatsoever, and the ellipses represent higher-order terms. Clearly the Hamiltonian defined in Eq. (2.4) is obtained by setting $S=$const, since then the generator commutes with all operators and only the zeroth-order terms survive.

As mentioned above the generator S is chosen such that interactions of the lowest order are eliminated from the calculation, in which case it obeys the relation

$$i[S,H_0]=H_{\text{int}}^A(\mathbf{k},\lambda)+H_{\text{int}}^B(\mathbf{k}',\lambda')$$

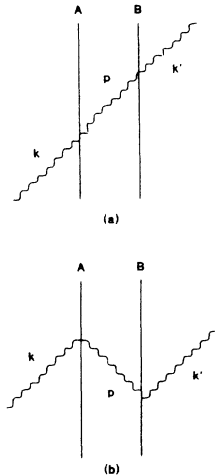$$=i[S^A,H_0]+i[S^B,H_0] . \qquad (2.9)$$

FIG. 3. Two collapsed time-ordered diagrams for a scattering event involving the annihilation of a laser photon at A and creation of a scattered photon at B.

With this choice of commutator, we find that Eq. (2.8) becomes

$$H = H_0 + H_{\text{int}}^A(\mathbf{p}, \epsilon) + H_{\text{int}}^B(\mathbf{p}, \epsilon)$$

$$- i\{[S, H_{\text{int}}^A(\mathbf{p}, \epsilon)] + [S, H_{\text{int}}^B(\mathbf{p}, \epsilon)] + [S, H_{\text{int}}^A(\mathbf{k}, \lambda)]$$

$$+ [S, H_{\text{int}}^B(\mathbf{k}', \lambda')]\} + \cdots , \qquad (2.10)$$

where the ellipsis represents higher-order terms. Equation (2.9) implies that the generator S is a function of the two interaction Hamiltonians $H^A(\mathbf{k}, \lambda)$ and $H^B(\mathbf{k}', \lambda')$, and this in turn implies that the last two commutators in Eq. (2.10) are second order in $H^A(\mathbf{k}, \lambda)$ and $H^B(\mathbf{k}', \lambda')$, and will therefore not contribute to the process under scrutiny. For similar reasons all higher-order terms are of little interest.

The next step in the calculation is to evaluate the generator S defined in Eq. (2.9). Assuming that the basis states are all orthonormal eigenfunctions of the Hamiltonian H_0, we find that

$$\langle 1(\mathbf{k}', \lambda'); r_B | S^B | s_B; 0(\mathbf{k}', \lambda) \rangle$$

$$= \frac{-i\langle (\mathbf{k}', \lambda'); r_B | H_{\text{int}}(\mathbf{k}', \lambda') | s_B; 0(\mathbf{k}', \lambda) \rangle}{E_{sr}^B - \hbar c k'} , \qquad (2.11)$$

where $E_{sr}^B = E_s^B - E_r^A$ and the state labels of A and the virtual photon have been suppressed since they appear unchanged at each end of the Dirac bracket; in writing Eq. (2.11) we have also assumed that there are no one-photon resonances. The result for the generator S^A is directly analogous to that above, and can be obtained by swapping the labels $B \rightarrow A$ and $k' \rightarrow -k$.

Having explicitly calculated the form of the generator S it is possible to obtain the form of the transformed interaction Hamiltonian. By substituting Eq. (2.11) and its counterpart of S^A into (2.10), we obtain the transformed Hamiltonian for the system. Note that the commutator terms $[S, H_{\text{int}}^A(\mathbf{p}, \epsilon)]$ and $[S, H_{\text{int}}^B(\mathbf{p}, \epsilon)]$ contain all necessary interaction terms to describe the cooperative process defined in Eqs. (2.5) and (2.6). We thus define two effective interaction contributions

$$H_{\text{eff}}(\mathbf{k}, \mathbf{k}') = -i\{[S^A, H_{\text{int}}^A(\mathbf{p}, \epsilon)] + [S^B, H_{\text{int}}^B(\mathbf{p}, \epsilon)]\}$$

$$= H_{\text{eff}}^A(\mathbf{k}) + H_{\text{eff}}^B(\mathbf{k}') . \qquad (2.12)$$

Operating on either side of Eq. (2.12) with the initial and final states of the system defined in Eqs. (2.3) and (2.4), we find that the matrix element for the effective Hamiltonian for the transition $|i\rangle \rightarrow |f\rangle$ is simply

$$\langle f | H_{\text{eff}}(\mathbf{k}, \mathbf{k}') | i \rangle = -\epsilon_0^{-2} \alpha_{ij}^A(k) d_j^{\perp}(\mathbf{p}) d_i^{\perp}(\mathbf{k})$$

$$- \epsilon_0^{-2} \alpha_{ij}^B(k') d_i^{\perp}(\mathbf{p}) d_j^{\perp}(\mathbf{k}') . \qquad (2.13)$$

Written in this form the meaning of the commutator terms is clear, since the rank-two tensors appearing in Eq. (2.13) are none other than the Raman polarizability tensors for molecules A and B, defined as

$$\alpha_{ij}^A(k) = \sum_r \left[\frac{\mu_i^{\alpha' r} \mu_j^{r\alpha}}{E_{r\alpha'} + \hbar c k} + \frac{\mu_j^{\alpha' r} \mu_i^{r\alpha}}{E_{r\alpha} - \hbar c k} \right] , \qquad (2.14)$$

$$\alpha_{ij}^B(k') = \sum_r \left[\frac{\mu_j^{\beta' r} \mu_i^{r\beta}}{E_{r\beta'} - \hbar c k'} + \frac{\mu_i^{\beta' r} \mu_j^{r\beta}}{E_{r\beta} + \hbar c k'} \right] . \qquad (2.15)$$

Using the effective interaction terms and applying second-order perturbation theory we find that

$$U(t, 0) = \frac{(i\hbar)^{-2}}{2!} T \left[\int_0^t dt_1 \int_0^t dt_2 H_{\text{eff}}^A(\mathbf{k}, t_1) H_{\text{eff}}^B(\mathbf{k}', t_2) \right]$$

$$= \frac{(i\hbar)^{-4}}{4!} T \left[\int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \int_0^t dt_4 H_{\text{int}}^A(\mathbf{k}, t_1) H_{\text{int}}^A(\mathbf{p}, t_2) H_{\text{int}}^B(\mathbf{p}, t_3) H_{\text{int}}^B(\mathbf{k}', t_4) \right] . \qquad (2.16)$$

This is an important result since it vindicates the description of cooperative Raman scattering by the collapsed time-ordered diagrams given in Fig. 3, in which each molecular center undergoes a scattering event involving a virtual photon.

Substitution of Eqs. (2.12)–(2.16) into (2.6) gives us the explicit form for the time-dependent probability amplitude. Carying out the necessary time integrations, applying closure, and performing the summation over the polarizations of the virtual states, leads to the result

$$c_{fi}(t) = \frac{e^{-i(\mathbf{k}'\cdot\mathbf{R}_b - \mathbf{k}\cdot\mathbf{R}_a)}}{4\epsilon_0^2 V^2}(nkk')^{1/2}\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times \sum_{p=0}^{\infty} p(\delta_{jk} - \hat{p}_j\hat{p}_k)\left[\frac{(e^{ict(K_\alpha + K_\beta)} - 1)e^{-i\mathbf{p}\cdot\mathbf{R}}}{(K_\alpha + K_\beta)(K_\beta + p)} - \frac{(e^{ict(K_\alpha - p)} - 1)e^{-i\mathbf{p}\cdot\mathbf{R}}}{(K_\alpha - p)(K_\beta + p)}\right.$$

$$\left. + \frac{(e^{ict(K_\alpha + K_\alpha)} - 1)e^{i\mathbf{p}\cdot\mathbf{R}}}{(K_\alpha + K_\beta)(K_\alpha + p)} - \frac{(e^{ict(K_\beta - p)} - 1)e^{i\mathbf{p}\cdot\mathbf{R}}}{(K_\beta - p)(K_\alpha + p)}\right], \tag{2.17}$$

where δ_{jk} is the Kronecker delta tensor, the vector $\mathbf{R} = (\mathbf{R}_b - \mathbf{R}_a)$ defines the location of center B with respect to A, and

$$K_\alpha = \frac{E_{\alpha'\alpha} - \hbar ck}{\hbar c}, \tag{2.18}$$

$$K_\beta = \frac{E_{\beta'\beta} + \hbar ck'}{\hbar c}. \tag{2.19}$$

In the conventional Fermi golden rule treatment,[29] the second and fourth terms within large parentheses in Eq. (2.17) are usually ignored, on the grounds that they are highly oscillatory, and that the sum over virtual states will therefore lead to a vanishing contribution. However, it is apparent that the poles in the denominators result in significant contributions whenever the energy of the virtual photon satisfies energy conservation for absorption or emission at each molecular center. Thus in cooperative processes the usual Fermi treatment has to be modified. In the limit of a large quantization volume, it is possible to replace the summation over all virtual states by an integral over p space. Care must be taken, however, since in the special case where molecule A remains in its ground state after cooperative procedure, stimulated emission and absorption processes favor a process where the virtual photon exists in the mode of the laser radiation. The corresponding term in the summation is then weighted with an additional factor of $n^{1/2}$ at each photon vertex. Consequently, on resorting to spherical polar coordinates, and carrying out angular integrations, we obtain

$$c_{fi}(t) = \frac{e^{-i(\mathbf{k}'\cdot\mathbf{R}_b - \mathbf{k}\cdot\mathbf{R}_a)}}{16\pi^2\epsilon_0^2 V}(nkk')^{1/2}\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times \int_0^\infty (-\nabla^2\delta_{jk} + \nabla_j\nabla_k)\frac{\sin(pR)}{iR}\left[\frac{(e^{ict(K_\alpha + K_\beta)} - 1)}{(K_\alpha + K_\beta)(K_\beta + p)} - \frac{(e^{ict(K_\alpha - p)} - 1)}{(K_\alpha - p)(K_\beta + p)}\right.$$

$$\left. + \frac{(e^{ict(K_\alpha + K_\beta)} - 1)}{(K_\alpha + K_\beta)(K_\alpha + p)} - \frac{(e^{ict(K_\beta - p)} - 1)}{(K_\beta - p)(K_\alpha + p)}\right]dp$$

$$+ \frac{e^{-i(\mathbf{k}'\cdot\mathbf{R}_b - \mathbf{k}\cdot\mathbf{R}_a)}}{4\epsilon_0^2 V^2}(n^3k^3k')^{1/2}\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')(\delta_{jk} - \hat{k}_j\hat{k}_k)$$

$$\times \left[\frac{(e^{ict(K_\alpha + K_\beta)} - 1)e^{i\mathbf{k}\cdot\mathbf{R}}}{(K_\alpha + K_\beta)(K_\beta + k)} - \frac{(e^{ict(K_\alpha - p)} - 1)e^{i\mathbf{k}\cdot\mathbf{R}}}{(K_\alpha - k)(K_\beta + k)} + \frac{(e^{ict(K_\alpha + K_\beta)} - 1)e^{-i\mathbf{k}\cdot\mathbf{R}}}{(K_\alpha + K_\beta)(K_\alpha + k)} - \frac{(e^{ict(K_\beta - p)} - 1)e^{-i\mathbf{k}\cdot\mathbf{R}}}{(K_\beta - k)(K_\alpha + k)}\right]. \tag{2.20}$$

The term involving $(n^3)^{1/2}$ corresponds to the stimulated emission-absorption case mentioned above. Over physically measurable time scales, this term will be of negligible importance unless the scattering at A is elastic; for the specifically inelastic scattering process considered in this paper, the term may be dropped.

In order to evaluate the integrals in p space, one notes that, on the energy shell $(K_\alpha = -K_\beta)$,

$$\int_0^\infty \frac{\sin(pR)}{iR} \times \left[\frac{(e^{ict(K_\alpha + K_\beta)} - 1)}{(K_\alpha + K_\beta)(K_\beta + p)} - \frac{(e^{ict(K_\alpha - p)} - 1)}{(K_\alpha - p)(K_\beta + p)} + \frac{(e^{ict(K_\alpha + K_\beta)} - 1)}{(K_\alpha + K_\beta)(K_\alpha + p)} - \frac{(e^{ict(K_\beta - p)} - 1)}{(K_\beta - p)(K_\alpha + p)}\right]dp$$

$$= \int_{-\infty}^\infty \frac{\sin(pR)}{iR}\left[\frac{(e^{ict(K_\alpha + K_\beta)} - 1)}{(K_\alpha + K_\beta)(K_\beta + p)} + \frac{1}{(K_\alpha - p)(K_\beta + p)}\right]dp$$

$$- \int_0^\infty \frac{\sin(pR)}{iR}\left[\frac{e^{ict(K_\alpha - p)}}{(K_\alpha - p)(K_\beta + p)} + \frac{e^{ict(K_\beta - p)}}{(K_\beta - p)(K_\alpha + p)}\right]dp.$$

Of the last two integrals the first term has no pole in the region of integration, and is highly oscillatory. This integral is very similar to that ignored in the Fermi golden-rule treatment of the second-order matrix element. This term averages to zero over periods of p that are sufficiently large, and is therefore ignored. The fourth integrand has two simple poles in the region of integration, and cannot be ignored. Noting that the principal contribution to this integral arises from the poles, it is possible to extend the limits of integration to $(-\infty, \infty)$ so long as we ignore all poles not previously included in the region $(0 \leq p \leq \infty)$. The integral involved is then easily solved by taking the Cauchy principal part.[19]

Performing the integration in Eq. (2.20) leads to the following result for $ct > R$:

$$c_{fi}(t) = \frac{e^{-i(\mathbf{k}'\cdot\mathbf{R}_b - \mathbf{k}\cdot\mathbf{R}_a)}}{8\pi^2\epsilon_0^2 V}(nkk')^{1/2}\alpha_{ij}^A(k)\alpha_{kl}^B(k')$$

$$\times e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')(-\nabla^2\delta_{jk} + \nabla_j\nabla_k)\frac{1}{R}$$

$$\times \frac{\pi e^{iK_\beta ct}}{(K_\alpha + K_\beta)}(e^{-iK_\alpha(R-ct)} - e^{iK_\beta(R-ct)}) . \quad (2.21)$$

The time-dependent probability $P_{fi}(t)$ is now given by the square modulus of the probability amplitude defined in Eq. (2.21), and is thus

$$P_{fi}(t) = \frac{(nkk')}{4\epsilon_0^2 V^2}\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')\bar{\alpha}_{mn}^A(k)\bar{\alpha}_{op}^B(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')$$

$$\times (4\pi\epsilon_0)^{-1}(-\nabla^2\delta_{jk} + \nabla_j\nabla_k)\frac{1}{R}(4\pi\epsilon_0)^{-1}(-\nabla'^2\delta_{no} + \nabla'_n\nabla'_o)\frac{1}{R'}$$

$$\times \frac{-1}{(K_\alpha + K_\beta)^2}(-2 + e^{-iK_\alpha(R'-ct)-iK_\beta(R-ct)} + e^{iK_\beta(R-ct)+iK_\alpha(R'-ct)}) . \quad (2.22)$$

Although the above result in principle represents the correct time-dependent probability for a scattering process from A to B, it in fact corresponds to a physically unrealistic case where there is no imprecision in the measurement of the wave vectors of either the laser or the scattered photons. In a normal Raman experiment, however, the photodetector subtends a finite solid angle at the scattering center, and the associated uncertainty in the wave vector of the scattered light is accounted for by summing over radiation modes within a small element of solid angle around $\mathbf{k}$.[30-33] As in the Fermi rule treatment, we convert this summation to an integral over $\mathbf{k}'$, noting that the energy conserving value for $|\mathbf{k}'|$ dominates at all times beyond the femtosecond regime. In fact, the long-time limit of the integrand is a δ function corresponding to exact energy conservation.[34,35] Since the integrand is highly oscillatory everywhere except at the pole $K_\beta = -K_\alpha$, the integral limits can be extended to $(-\infty, \infty)$, and the variable of integration changed to K_β. taking the principal part of the integral leads to a physically measured probability that comprises outgoing waves only, i.e.,

$$\bar{P}_{fi}(t) = \frac{(nkk')\hbar c}{4\epsilon_0^2 V^2}\rho_{k'}\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times \bar{\alpha}_{mn}^A(k)\bar{\alpha}_{op}^B(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')(4\pi\epsilon_0)^{-1}$$

$$\times (-\nabla^2\delta_{jk} + \nabla_j\nabla_k)\frac{1}{R}(4\pi\epsilon_0)^{-1}$$

$$\times (-\nabla'^2\delta_{no} + \nabla'_n\nabla'_o)\frac{1}{R'}2\pi cte^{iK(R-R')} , \quad (2.23)$$

where $\rho_{k'}$ is the density of scattered radiation modes

$$\rho_{k'} = \frac{k'^2 V d\Omega}{(2\pi)^3\hbar c} , \quad (2.24)$$

and the pole ensures that the energy conservation condition $K_\beta = -K_\alpha = K$ is obeyed.

The rate of differential scattering into an element of solid angle $d\Omega$ about the direction $\mathbf{k}'$ is obtained by differentiating equation (2.23) with respect to t. More usefully the result can be recast in terms of a radiant scattering intensity $I_{fi}(k')$, defined as the Raman scattering energy radiated in the direction of $\mathbf{k}'$ per unit solid angle per unit time,

$$I_{fi}(k') = \frac{I(k)k'^4}{(4\pi\epsilon_0)^2}\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')\bar{\alpha}_{mn}^A(k)$$

$$\times \bar{\alpha}_{op}^B(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')(4\pi\epsilon_0)^{-1}$$

$$\times (-\nabla^2\delta_{jk} + \nabla_j\nabla_k)\frac{1}{R}(4\pi\epsilon_0)^{-1}$$

$$\times (-\nabla'^2\delta_{no} + \nabla'_n\nabla'_o)\frac{1}{R'}e^{iK(R-R')} , \quad (2.25)$$

where $I(k)$ is the irradiance of the incident laser beam for the mode k. Operating on the Green's functions with the differential operators gives the result[36]

$$(4\pi\epsilon_0)^{-1}(-\nabla^2\delta_{jk}+\nabla_j\nabla_k)\frac{1}{R}\exp(iKR)$$

$$=V_{jk}(K,\mathbf{R})=\frac{1}{4\pi\epsilon_0R^3}(\{(\delta_{jk}-3\hat{R}_j\hat{R}_k)[\cos(KR)+KR\sin(KR)]-(\delta_{jk}-\hat{R}_j\hat{R}_k)[K^2R^2\cos(KR)]\}$$

$$+i\{(\delta_{jk}-3\hat{R}_j\hat{R}_k)[\sin(KR)-KR\cos(KR)]-(\delta_{jk}-\hat{R}_j\hat{R}_k)[K^2R^2\sin(KR)]\}),\tag{2.26}$$

where $V_{jk}(K,\mathbf{R})$ is the polarization-summed complex retarded interaction tensor. This is often referred to as the photon propagator for a photon traveling between the two molecular centers,[9] or the tensor field.[8] It is of direct interest to consider the physics of the above results for a pair of interacting molecules. In this case the term $V_{jk}(K,\mathbf{R})\bar{V}_{no}(K',\mathbf{R})$ has the form

$$V_{jk}(K,\mathbf{R})\bar{V}_{no}(K,\mathbf{R})=\frac{1}{16\pi^2\epsilon_0^2R^6}\{(\delta_{jk}-3\hat{R}_j\hat{R}_k)(\delta_{no}-3\hat{R}_n\hat{R}_o)(1+K^2R^2)$$

$$-[(\delta_{jk}-3\hat{R}_j\hat{R}_k)(\delta_{no}-\hat{R}_n\hat{R}_o)+(\delta_{jk}-\hat{R}_j\hat{R}_k)(\delta_{no}-3\hat{R}_n\hat{R}_o)]K^2R^2$$

$$+(\delta_{jk}-\hat{R}_j\hat{R}_k)(\delta_{no}-\hat{R}_n\hat{R}_o)K^4R^4\}.\tag{2.27}$$

In the limit where the intermolecular separation is small, only the first term in the above expression contributes to the intensity. Substitution of this term into Eq. (2.25) simply gives the familiar longitudinal induced-dipole–induced-dipole result for the scattering intensity.

In the long-range limit we find that the last term in Eq. (2.27) is the dominant term. This result is simply that for a process where a real photon scattered at A is subsequently scattered at site B. The quantum electrodynamical result given in Eq. (2.25) thus shows how multiple inelastic scattering and induced-dipole–induced-dipole scattering are in fact merely the long- and short-range limits of a unified theory of cooperative Raman scattering, involving intermolecular virtual-photon energy transfer.

In the discussion so far, the theory has been concerned with a cooperative scattering process in which the incident laser photon is annihilated at A, and the scattered photon is created at site B. Equation (2.25) therefore gives the intensity for light cooperatively scattered from one molecular center (site B). In any complete calculation, however, the converse case, where the laser photon is annihilated at B and the scattered photon is created at A, must also be accounted for. The observed intensity for pairwise scattering is consequently given by the sum of the two probability amplitudes obtained in Eq. (2.21). By following the procedure outlined in Eqs. (2.22)–(2.26) we obtain the concomitant result for the observed Raman scattering intensity,

$$I_{fi}(k')=\frac{I(k)k'^4}{(4\pi\epsilon_0)^2}\{\alpha_{ij}^A(k)\alpha_{kl}^B(k')\bar{\alpha}_{mn}^A(k)\bar{\alpha}_{op}^B(k')e_i(\mathbf{k})\bar{e}_l'(\mathbf{k}')\bar{e}_m(\mathbf{k})e_p'(\mathbf{k}')V_{jk}(K,\mathbf{R})\bar{V}_{no}(K,\mathbf{R})$$

$$+\alpha_{ij}^A(k')\alpha_{kl}^B(k)\bar{\alpha}_{mn}^A(k')\bar{\alpha}_{op}^B(k)e_k(\mathbf{k})\bar{e}_j'(\mathbf{k}')\bar{e}_o(\mathbf{k})e_n'(\mathbf{k}')V_{li}(K',\mathbf{R})\bar{V}_{pm}(K',\mathbf{R})$$

$$+\alpha_{ij}^A(k)\alpha_{kl}^B(k')\bar{\alpha}_{mn}^A(k')\bar{\alpha}_{op}^B(k)e_i(\mathbf{k})\bar{e}_1'(\mathbf{k}')\bar{e}_o(\mathbf{k})e_n'(\mathbf{k}')V_{jk}(K,\mathbf{R})\bar{V}_{pm}(K',\mathbf{R})$$

$$\times\exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]+\alpha_{ij}^A(k')\alpha_{kl}^B(k)\bar{\alpha}_{mn}^A(k)\bar{\alpha}_{op}^B(k')e_k(\mathbf{k})\bar{e}_j'(\mathbf{k}')\bar{e}_m(\mathbf{k})$$

$$\times e_p'(\mathbf{k}')V_{jk}(K',\mathbf{R})\bar{V}_{no}(K,\mathbf{R})\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]\},\tag{2.28}$$

where $K'=(E_{\alpha'\alpha}+\hbar ck')/\hbar c$. An interesting feature of Eq. (2.28) is the appearance of interference terms characterized by exponential phase factors. These terms arise as a result of quantum-mechanical interference between the probability amplitudes for cooperative Raman scattering from center A to center B, and from B to A. Such terms will only contribute when both molecules are within the interaction volume of the laser. As we shall see later, the inclusion of these phase factors in the interference terms can lead to a circular differential Raman effect.

As it stands, Eq. (2.28) is applicable to systems where the A-B pair is held in a fixed orientation with respect to the laser light. The theory should thus allow one to describe, for example, the effects of bimolecular scattering

in matrix-isolated species. In the special case of solids Raman scattering is best treated as a many-body problem within a full multipolar, or minimal coupling framework.[37–39] In the theory to be developed below, we concentrate on the wider issues of pairwise scattering in fluids, where higher-order scattering mechanisms are statistically of little significance. This can lead to two types of behavior. The first occurs when chromophores within the same molecule undergo a cooperative scattering process. This process of *intramolecular* scattering may be observed in large molecules where chromophores outside the range of orbital overlap interact through induced dipole-induced dipole coupling. The second type of behavior that may be exhibited occurs when chromophores

on *different* molecules undergo pairwise, or *bimolecular* scattering. In this case, studies of such behavior could access new information as to the nature of solvent-solute interactions.

III. COOPERATIVE SCATTERING IN FLUIDS

A. Intramolecular scattering

In this section we consider the case where an A-B chromophore system with fixed *mutual* orientation is free to rotate in the laser beam. The results to be derived are therefore applicable to scattering processes where the centers A and B refer to chromophores within a molecule, van der Waals molecule, or ligands within a crystal field or coordination shell. In order to calculate the observed rate for the intramolecular scattering for an ensemble it is necessary to effect an orientational average. This is achieved by first specifying a laboratory-fixed Cartesian frame into which all polarization vectors are cast, related to the molecular frame by the usual Euler angle matrix. If we do this we can write the rotational average of (2.27) as

$$I_{fi}(k') = \frac{I(k)k'^4}{(4\pi\epsilon_0)^2}\{\alpha^A_{\lambda\mu}(k)\alpha^B_{vo}(k')\bar{\alpha}^A_{\rho\sigma}(k)\bar{\alpha}^B_{\tau\theta}(k')e_i(k)\bar{e}'_i(k')\bar{e}_m(k)e'_p(k')V_{\mu v}(K,R)\bar{V}_{\sigma\tau}(K,R)\langle l_{\lambda i}l_{ol}l_{pm}l_{\theta p}\rangle$$

$$+\alpha^A_{\lambda\mu}(k')\alpha^B_{vo}(k)\bar{\alpha}^A_{\rho\sigma}(k')\bar{\alpha}^B_{\tau\theta}(k)e_i(k)\bar{e}'_i(k')\bar{e}_m(k)e'_p(k')V_{o\lambda}(K',R)\bar{V}_{\theta\rho}(K',R)\langle l_{iv}l_{l\mu}l_{m\tau}l_{p\sigma}\rangle$$

$$+\alpha^A_{\lambda\mu}(k)\alpha^B_{vo}(k')\bar{\alpha}^A_{\rho\sigma}(k)\bar{\alpha}^B_{\tau\theta}(k)e_i(k)\bar{e}'_i(k')\bar{e}_m(k)e'_p(k')V_{\mu v}(K,R)\bar{V}_{\theta\sigma}(K',R)$$

$$\times\langle l_{i\lambda}l_{lo}l_{m\tau}l_{p\sigma}\exp[-i(k-k')\cdot R]\rangle$$

$$+\alpha^A_{\lambda\mu}(k')\alpha^B_{vo}(k)\bar{\alpha}^A_{\rho\sigma}(k)\bar{\alpha}^B_{\tau\theta}(k')e_i(k)\bar{e}'_i(k')\bar{e}_m(k)e'_p(k')V_{o\lambda}(K',R)\bar{V}_{\sigma\tau}(K,R)$$

$$\times\langle l_{iv}l_{l\mu}l_{m\rho}l_{p\theta}\exp[i(k-k')\cdot R]\rangle\} \tag{3.1}$$

where the angular brackets denote the need for a rotational average, and where $l_{j\mu}$ is the direction cosine between the j axis of the laboratory frame and the μ axis of the molecule-fixed frame.

While the rotational averages can be calculated via direct integration over the Euler angles, the results are more readily obtained through use of irreducible Cartesian tensor methods which cast the sets of contracted polarization tensors in a form directly amenable for use.[40–42] The first two terms in Eq. (3.1) require a straightforward fourth-rank isotropic average of the type outlined in Refs. 40 and 42, while the last two terms include orientationally dependent phase factors and therefore require the utilization of fourth-rank phased averages given in Ref. 41. Assuming that intramolecular coupling is the predominant mechanism, and that bimolecular scattering is negligible, the result obtained by explicitly evaluating these averages can be written concisely in the following form:

$$I_{fi}(k') = C\left[\sum_{j=0}^{4}\sum_{p,q=1}^{N_4^{(j)}}\frac{(2j)!}{2^j(j!)^2}i^jj_j(|k-k'|R)g^{pq}_{\{4;j\}}A^{(j;q)}[T^{(j;p)}(A,B;K,K')+(-1)^jT^{(j;p)}(A\leftrightarrow B;K\leftrightarrow K')]\right.$$

$$+\sum_{p,q}g^{pq}_{\{4;0\}}A^{(0;q)}[S^{(0;p)}(K,K')+S^{(0;p)}(A\leftrightarrow B;K\leftrightarrow K')]\right], \tag{3.2}$$

where

$$C=\left[\frac{I(k)k'^4}{(4\pi\epsilon_0)^2}\right], \tag{3.3}$$

and where $j_j(|k-k'|R)$ is a spherical Bessel function of order j; $g_{(4;j)}$ is the rank-four, weight-j, tensor metric, tabulated in the literature,[43] and $N_4^{(j)}$ the multiplicity of

the weight-j representation in the rank-four tensor subspace given by[44]

$$N_n^{(j)}=\sum_k(-1)^k\begin{bmatrix}n\\k\end{bmatrix}\begin{bmatrix}2n-3k-j-1\\n-2\end{bmatrix}, \tag{3.4}$$

where $0\le k\le[(n-j)/3]$. The tensor invariants $A^{(j;q)}$, $S^{(0;p)}$, and $T^{(j;p)}$ are contracted sets of polarization vec-

TABLE I. Explicit forms for the polarization and molecular response invariants.

j	p	$A^{(j;p)}$
0	1	$(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}')$
0	2	1
0	3	$(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}')$
1	1	$(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{e}\times\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}')$
1	2	$(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{e}\times\bar{\mathbf{e}})(\mathbf{e}'\cdot\bar{\mathbf{e}}')$
1	3	$(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{e}\times\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}')$
1	4	$(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}'\times\bar{\mathbf{e}})(\mathbf{e}\cdot\mathbf{e}')$
1	5	$(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}'\times\mathbf{e}')(\mathbf{e}\cdot\bar{\mathbf{e}})$
1	6	$(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}\times\mathbf{e}')(\mathbf{e}\cdot\bar{\mathbf{e}}')$
2	1	$(\mathbf{e}\cdot\bar{\mathbf{e}}')[\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')\bar{\mathbf{e}}\cdot(\mathbf{k}-\mathbf{k}')-\frac{1}{3}(\bar{\mathbf{e}}\cdot\mathbf{e}')]$
2	2	$[|\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')|^2-\frac{1}{3}]$
2	3	$(\mathbf{e}\cdot\mathbf{e}')[\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')\bar{\mathbf{e}}\cdot(\mathbf{k}-\mathbf{k}')-\frac{1}{3}(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}')]$
2	4	$(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}')[\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')-\frac{1}{3}(\mathbf{e}\cdot\mathbf{e}')]$
2	5	$[|\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')|^2-\frac{1}{3}]$
2	6	$(\bar{\mathbf{e}}\cdot\mathbf{e}')[\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')e\cdot(\mathbf{k}-\mathbf{k}')-\frac{1}{3}(\mathbf{e}\cdot\bar{\mathbf{e}}')]$
3	1	$\{(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{e}\times\bar{\mathbf{e}})|\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')|^2$ $-\frac{1}{5}[\bar{\mathbf{e}}'\cdot(\mathbf{e}\times\bar{\mathbf{e}})\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')+\mathbf{e}'\cdot(\mathbf{e}\times\bar{\mathbf{e}})\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')+(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{e}\times\bar{\mathbf{e}})]\}$
3	2	$\{(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}'\times\bar{\mathbf{e}})\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')$ $-\frac{1}{5}[\mathbf{e}\cdot(\bar{\mathbf{e}}'\times\bar{\mathbf{e}})\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')+\mathbf{e}'\cdot(\bar{\mathbf{e}}'\times\bar{\mathbf{e}})\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')+(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}'\times\bar{\mathbf{e}})(\mathbf{e}\cdot\mathbf{e}')]\}$
3	3	$\{(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}\times\mathbf{e}')\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')$ $-\frac{1}{5}[\mathbf{e}\cdot(\bar{\mathbf{e}}\times\mathbf{e}')\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')+\bar{\mathbf{e}}'\cdot(\bar{\mathbf{e}}\times\mathbf{e}')\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')+(\mathbf{k}-\mathbf{k}')\cdot(\bar{\mathbf{e}}\times\mathbf{e}')(\mathbf{e}\cdot\bar{\mathbf{e}}')]\}$
4	1	$\{\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')\bar{\mathbf{e}}\cdot(\mathbf{k}-\mathbf{k}')\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')$ $-\frac{1}{7}[(\mathbf{e}\cdot\bar{\mathbf{e}}')\bar{\mathbf{e}}\cdot(\mathbf{k}-\mathbf{k}')\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')+|\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')|^2+(\mathbf{e}\cdot\mathbf{e}')\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')\bar{\mathbf{e}}\cdot(\mathbf{k}-\mathbf{k}')$ $+(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}')\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')\mathbf{e}'\cdot(\mathbf{k}-\mathbf{k}')+|\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')|^2+(\bar{\mathbf{e}}\cdot\mathbf{e}')\bar{\mathbf{e}}'\cdot(\mathbf{k}-\mathbf{k}')\mathbf{e}\cdot(\mathbf{k}-\mathbf{k}')]$ $+\frac{1}{35}[(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}')+1+(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}')]\}$

j	p	$S^{(0;p)}(A,B;\gamma,\gamma')$
0	1	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega)\bar{\alpha}^B_{\lambda_7\lambda_5}(\omega')V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_6\lambda_7}(\gamma)$
0	2	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_1\lambda_6}(\omega)\bar{\alpha}^B_{\lambda_7\lambda_4}(\omega')V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_6\lambda_7}(\gamma)$
0	3	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_4\lambda_6}(\omega)\bar{\alpha}^B_{\lambda_7\lambda_1}(\omega')V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_6\lambda_7}(\gamma)$

j	p	$T^{(j;p)}(A,B;\gamma,\gamma')$
0	1	$V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\gamma\lambda_8}(\gamma')\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\alpha^B_{\lambda_6\lambda_8}(\omega)$
0	2	$V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_1\lambda_8}(\omega)$
0	3	$V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega')\bar{\alpha}^B_{\lambda_4\lambda_8}(\omega)$
1	1	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega)\bar{\alpha}^B_{\lambda_6\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_5\lambda_8}(\gamma')\epsilon_{\lambda_1\lambda_4\lambda_\tau}\hat{R}_{\lambda_\tau}$
1	2	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_5\lambda_8}(\gamma')\epsilon_{\lambda_1\lambda_7\lambda_\tau}\hat{R}_{\lambda_\tau}$
1	3	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega)\bar{\alpha}^B_{\lambda_4\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_5\lambda_8}(\gamma')\epsilon_{\lambda_1\lambda_6\lambda_\tau}\hat{R}_{\lambda_\tau}$
1	4	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega)\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_5\lambda_8}(\gamma')\epsilon_{\lambda_4\lambda_7\lambda_\tau}\hat{R}_{\lambda_\tau}$
1	5	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_1\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_5\lambda_8}(\gamma')\epsilon_{\lambda_4\lambda_6\lambda_\tau}\hat{R}_{\lambda_\tau}$
1	6	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega)\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)\bar{V}_{\lambda_5\lambda_8}(\gamma')\epsilon_{\lambda_7\lambda_6\lambda_\tau}\hat{R}_{\lambda_\tau}$
2	1	$\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')$ $\times[\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_7}\hat{R}_{\lambda_6}-\frac{1}{3}\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_6\lambda_8}(\omega)]$

TABLE I. (*Continued*).

j	p	$A^{(j;p)}$
2	2	$\alpha^A_{\lambda_1\lambda_2}(\omega)\bar{\alpha}^B_{\lambda_1\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')$ $\times[\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\hat{R}_{\lambda_4}\hat{R}_{\lambda_6}-\frac{1}{3}\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')]$
2	3	$\alpha^A_{\lambda_1\lambda_2}(\omega)\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega')V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\gamma_8}(\gamma')$ $\times[\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_4}\hat{R}_{\lambda_7}-\frac{1}{3}\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_4\lambda_8}(\omega)]$
2	4	$\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_4\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')$ $\times[\alpha^A_{\lambda_1\lambda_2}(\omega)\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\hat{R}_{\lambda_1}\hat{R}_{\lambda_6}-\frac{1}{3}\alpha^A_{\lambda_1\lambda_2}(\omega)\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega')]$
2	5	$\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')$ $\times[\alpha^A_{\lambda_1\lambda_2}(\omega)\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_7}-\frac{1}{3}\alpha^A_{\lambda_1\lambda_2}(\omega)\bar{\alpha}^B_{\lambda_1\lambda_8}(\omega)]$
2	6	$\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_6\lambda_8}(\omega)V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')$ $\times[\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\hat{R}_{\lambda_1}\hat{R}_{\lambda_4}-\frac{1}{3}\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')]$
3	1	$\epsilon_{\lambda_1\lambda_7\lambda_\tau}V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')\{\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_4}\hat{R}_{\lambda_6}\hat{R}_{\lambda_\tau}$ $-\frac{1}{5}[\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^{BV}_{\lambda_3\lambda_\tau}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_6}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_\tau}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_4}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_2\lambda_8}(\omega)\hat{R}_{\lambda_\tau}]\}$
3	2	$\epsilon_{\lambda_4\lambda_7\lambda_\tau}V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')\{\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_6}\hat{R}_{\lambda_\tau}$ $-\frac{1}{5}[\alpha^A_{\lambda_\tau\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_6}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_\tau}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_\tau}]\}$
3	3	$\epsilon_{\lambda_7\lambda_6\lambda_\tau}V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')\{\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_4}\hat{R}_{\lambda_\tau}$ $-\frac{1}{5}[\alpha^A_{\lambda_\tau\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_4}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_\tau}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_\tau}]\}$
4	1	$V_{\lambda_2\lambda_3}(\gamma)V_{\lambda_5\lambda_8}(\gamma')\{\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_4}\hat{R}_{\lambda_6}\hat{R}_{\lambda_7}$ $-\frac{1}{7}[\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_1\lambda_8}(\omega)\hat{R}_{\lambda_4}\hat{R}_{\lambda_6}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_4}\hat{R}_{\lambda_7}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_4\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_6}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_7}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_6\lambda_8}(\omega)\hat{R}_{\lambda_1}\hat{R}_{\lambda_4}$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_7\lambda_8}(\omega)\hat{R}_{\lambda_6}\hat{R}_{\lambda_7}]$ $+\frac{1}{35}[\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_1}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_6}(\omega')\bar{\alpha}^B_{\lambda_6\lambda_8}(\omega)$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_4}(\omega')\bar{\alpha}^B_{\lambda_1\lambda_8}(\omega)$ $+\alpha^A_{\lambda_1\lambda_2}(\omega)\alpha^B_{\lambda_3\lambda_4}(\omega')\bar{\alpha}^A_{\lambda_5\lambda_1}(\omega')\bar{\alpha}^B_{\lambda_4\lambda_8}(\omega)]\}$

tors and molecular tensors, respectively, explicitly defined in Table I.

The short- and long-range behavior of the result expressed by Eq. (3.2) and its polarization properties are examined in more detail in Secs. IV and V, respectively.

B. Bimolecular scattering

In the intermolecular coupling regime the problem is significantly more complicated, since one needs to perform a distribution average for the fluid. The starting point for the theory is Eq. (3.2), where the random orientation of the *A-B* pair with respect to the radiation field is already accounted for. For a system where the two centers are chemically identical and free to rotate with respect to one another, one has to replace the $T^{(j;p)}(A,B;K,K')$, $T^{(j;p)}(A\leftrightarrow B;K\leftrightarrow K')$, $S^{(0;p)}(A,B;K,K')$, and $S^{(0;p)}(A\leftrightarrow B;K\leftrightarrow K')$ terms by their isotropic averages $\langle\langle T^{(j;p)}(\mathbf{R}_A,\mathbf{R}_B;K,K')\rangle\rangle$, $\langle\langle T^{(j;p)}(\mathbf{R}_A\leftrightarrow\mathbf{R}_B;K\leftrightarrow K')\rangle\rangle$, $\langle\langle S^{(0;p)}(\mathbf{R}_A,\mathbf{R}_B;K,K')\rangle\rangle$, and $\langle\langle S^{(0;p)}(\mathbf{R}_A\leftrightarrow\mathbf{R}_B;K\leftrightarrow K')\rangle\rangle$. The replacement $\mathbf{R}_A$ for *A*, etc., reflects the fact that, for a unicomponent

fluid, each molecule is now only distinguishable via its position vector $\mathbf{R}$. The procedure for the further orientational averaging denoted by the double angular brackets is now as follows. First an average of species A with respect to B and the intermolecular displacement vector is required, followed by a further average of the B species with respect to the propagator, to account for the fact that the molecule A may be positioned anywhere on the surface of a sphere of radius R around B. The nature of this procedure is outlined elsewhere.[45]

The total intensity of intermolecular scattering from a

point $\mathbf{R}_1$ within the fluid is obtained by summing the rates for the coupling of A with all B molecules within the interaction volume of the laser. Following convention, one defines the polarization density at a point $\mathbf{R}_1$ within the fluid as[9]

$$\alpha_{ij}(k,R_a)\alpha_{mn}(k,R_a)=\int_{-\infty}^{\infty}d^3\mathbf{R}_1\alpha_{ij}(k,R_1)\alpha_{mn}(k,R_1)$$
$$\times\delta(\mathbf{R}_1-\mathbf{R}_a) . \qquad (3.5)$$

The intensity of bimolecular cooperative scattering at R_1 is then given as

$$I_{fi}(k')=\frac{C}{2}\int_{-\infty}^{\infty}d^3\mathbf{R}_1\left[\sum_{j=0}^{4}\sum_{p,q}\sum_{A,B}^{N_4^{(J)}}\frac{(2j)!}{2^j(j!)^2}i^jj_j(|\mathbf{k}-\mathbf{k}'|R)g_{(4;j)}^{pq}A^{(j;p)}\right.$$

$$\times\langle\delta(\mathbf{R}_A-\mathbf{R}_1)[\langle\!\langle T^{(j;p)}(\mathbf{R}_1,\mathbf{R}_B;K,K')\rangle\!\rangle$$

$$+(-1)^j\langle\!\langle T^{(j;p)}(\mathbf{R}_1\leftrightarrow\mathbf{R}_B;K\leftrightarrow K')\rangle\!\rangle]$$

$$\left.+\sum_{p,q}g_{(4;0)}^{pq}A^{(0;q)}[\langle\!\langle S^{(0;p)}(\mathbf{R}_1,\mathbf{R}_B;K,K')\rangle\!\rangle+\langle\!\langle S^{(0;p)}(\mathbf{R}_1\leftrightarrow\mathbf{R}_B;K\leftrightarrow K')\rangle\!\rangle]\rangle_d\right] . \qquad (3.6)$$

In Eq. (3.6) the angular brackets with the subscript d refer to a distributional average, and the factor $\frac{1}{2}$ is introduced to compensate for the fact that we count each pair of molecules twice when summing over both A and B. Since cooperative scattering is an incoherent process (i.e., the intensity is proportional to the sum of the squares of the probability amplitudes for each pair), the coherent four-body contributions are only nonzero for forward elastic scattering. (The proof of this is lengthy, and may be found in the Appendix to this paper.) Using the following identities for a one-component fluid,

$$\int_{-\infty}^{\infty}d^3\mathbf{R}_2\delta(\mathbf{R}_B-\mathbf{R}_2)f(\mathbf{R}_2)=f(\mathbf{R}_B) , \qquad (3.7)$$

$$\rho=\left\langle\sum_B\delta(\mathbf{R}_1-\mathbf{R}_B)\right\rangle , \qquad (3.8)$$

and

$$\left\langle\sum_A\sum_{B(\neq A)}\delta(\mathbf{R}_1-\mathbf{R}_A)\delta(\mathbf{R}_2-\mathbf{R}_B)\right\rangle=\rho^2 g(\mathbf{R}_1-\mathbf{R}_2) , \qquad (3.9)$$

where ρ is the number density and $g(\mathbf{R})$ is the pair correlation function for the fluid, it is possible to reduce Eq. (3.2) to

$$I_{fi}(k')=\frac{C}{2}\int_{-\infty}^{\infty}d^3\mathbf{R}_1\left[\rho^2\sum_{j=0}^{4}\sum_{p,q=1}^{N_4^{(j)}}\frac{(2j)!}{2^j(j!)^2}i^jj_j(|\mathbf{k}-\mathbf{k}'|R)g_{(4;j)}^{pq}A^{(j;p)}\right.$$

$$\times\int_{-\infty}^{\infty}g(\mathbf{R}_1-\mathbf{R}_2)[\langle\!\langle T^{(j;p)}(\mathbf{R}_1,\mathbf{R}_2;K,K')\rangle\!\rangle$$

$$+(-1)^j\langle\!\langle T^{(j;p)}(\mathbf{R}_1\leftrightarrow\mathbf{R}_2;K\leftrightarrow K')\rangle\!\rangle]d^3\mathbf{R}_2$$

$$+\sum_{p,q}g_{(4;0)}^{pq}A^{(0;q)}\int_{-\infty}^{\infty}g(\mathbf{R}_1-\mathbf{R}_2)[\langle\!\langle S^{(0;p)}(\mathbf{R}_1,\mathbf{R}_2;K,K')\rangle\!\rangle$$

$$\left.+\langle\!\langle S^{(0;p)}(\mathbf{R}_1\leftrightarrow\mathbf{R}_2;K\leftrightarrow K')\rangle\!\rangle]d^3\mathbf{R}_2\right] . \qquad (3.10)$$

Convoluting the integrals in Eq. (3.10) makes it possible to express the distance dependence of the integrands solely in terms of the integration variable $\mathbf{R}=\mathbf{R}_1-\mathbf{R}_2$. Using this property of the integral finally gives for the overall bimolecular Raman scattering intensity

$$I_{fi}(k')=2\pi C\rho^2 V_I\left[\sum_{j=0}^{4}\sum_{p,q=1}^{N_4^{(J)}}\frac{(2j)!}{2^j(j!)^2}i^jj_j(|\mathbf{k}-\mathbf{k}'|R)g_{(4;j)}^{pq}A^{(j;p)}\right.$$

$$\times\int_0^{\infty}R^2g(R)[\langle\!\langle T^{(j;p)}(R;K,K')\rangle\!\rangle+(-1)^j\langle\!\langle T^{(j;p)}(R;K\leftrightarrow K')\rangle\!\rangle]dR$$

$$\left.+\sum_{p,q}g_{(4;0)}^{pq}A^{(0;q)}\int_0^{\infty}R^2g(R)[\langle\!\langle S^{(0;p)}(R;K,K')\rangle\!\rangle+\langle\!\langle S^{(0;p)}(R;K\leftrightarrow K')\rangle\!\rangle]dR\right] , \qquad (3.11)$$

where V_I is the interaction volume of the laser. This is the result for intermolecular scattering within a one-component fluid. In this equation evaluation of the angular parts of the integrations has been facilitated by exploiting the isotropic nature of the integrands.

One-component systems can produce interesting features whereby the bimolecular scattering process provides a mechanism for the appearance of combination and overtone bands even in the case of a simple harmonic molecular force field. Chemically more interesting is the case where bimolecular scattering occurs between two chemically distinct species A and B. Here the resultant

combination bands clearly cannot be accessed by any unimolecular scattering mechanism. In this instance we must replace the pair correlation function defined in Eq. (3.9) by[9]

$$\left\langle \sum_{a \in A} \sum_{b \in B} \delta(\mathbf{R}_1 - \mathbf{R}_a)\delta(\mathbf{R}_2 - \mathbf{R}_b)\right\rangle = \rho_A \rho_B g^{AB}(\mathbf{R}_1 - \mathbf{R}_2) ,$$

(3.12)

where the summations over a and b represent inclusion of contributions from all molecules of types A and B, and ρ_A and ρ_B are the number densities of A and B species, respectively. The scattering intensity now becomes

$$
\begin{aligned}
I_{fi}(k') = 2\pi C \rho^A \rho^B V_I \Bigg[& \sum_{j=0}^{4} \sum_{p,q=1}^{N_4^{(J)}} \frac{(2j)!}{2^j(j!)^2} i^j j_j(|\mathbf{k} - \mathbf{k}'|R) g_{\{4;j\}}^{pq} A^{(j;p)} \\
& \times \int_{-\infty}^{\infty} R^2 g^{AB}(R)[\langle\!\langle T^{(j;p)}(A,B;R;K,K')\rangle\!\rangle \\
& \qquad\qquad + (-1)^j \langle\!\langle T^{(j;p)}(A,B;R;K\leftrightarrow K')\rangle\!\rangle]dR \\
& + \sum_{p,q} g_{\{4;0\}}^{pq} A^{(0;q)} \int_{-\infty}^{\infty} R^2 g^{AB}(R)[\langle\!\langle S^{(0;p)}(A,B;R;K,K')\rangle\!\rangle \\
& \qquad\qquad + \langle\!\langle S^{(0;p)}(A,B;R;K\leftrightarrow K')\rangle\!\rangle]dR \Bigg] .
\end{aligned}
$$

(3.13)

The process is now directly proportional to the densities of each component in the system.

IV. DEPENDENCE ON THE PAIR SEPARATION

A unique feature of cooperative scattering processes is the detailed nature of the scattering intensity dependence upon the relative displacement of the two chemical centers. In this section the explicit pair separation dependence is examined in more detail. It is possible to identify two limiting cases which are of particular interest, corresponding to *near*-zone and *far*-zone behavior.

A. Near zone

Physically the most important regime is that in which $|K|R$, $|K'|R$, and $|\mathbf{k} - \mathbf{k}'|R$ are significantly less than 1. In general, the appropriate short-range limits of the equations given in the previous section produce a significant simplification since all Bessel functions except those of zeroth-order become vanishingly small. Using the results obtained for a chromophore pair, we find that only the isotropic unweighted terms survive and the rate equation in the near zone becomes the following.

1. Chromophore pair

$$
I_{fi}(k') = \frac{C}{30} \begin{bmatrix} (\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}') \\ (\mathbf{e}\cdot\mathbf{e}')^1(\bar{\mathbf{e}}\cdot\bar{\mathbf{e}}') \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix}
$$

$$
\times \begin{vmatrix} \alpha_{\lambda_1\lambda_2}^A(\omega)\alpha_{\lambda_3\lambda_1}^B(\omega')V_{\lambda_2\lambda_3}(K)[\bar{\alpha}_{\lambda_5\lambda_6}^A(\omega)\bar{\alpha}_{\lambda_7\lambda_5}^B(\omega')\bar{V}_{\lambda_6\lambda_7}(K) + \bar{\alpha}_{\lambda_5\lambda_6}^A(\omega')\bar{\alpha}_{\lambda_6\lambda_6}^B(\omega)\bar{V}_{\lambda_5\lambda_6}(K')] \\ \alpha_{\lambda_1\lambda_2}^A(\omega)\alpha_{\lambda_3\lambda_4}^B(\omega')V_{\lambda_2\lambda_3}(K)[\bar{\alpha}_{\lambda_1\lambda_6}^A(\omega)\bar{\alpha}_{\lambda_7\lambda_4}^B(\omega')\bar{V}_{\lambda_6\lambda_7}(K) + \bar{\alpha}_{\lambda_5\lambda_1}^A(\omega')\bar{\alpha}_{\lambda_4\lambda_8}^B(\omega)\bar{V}_{\lambda_5\lambda_8}(K')] \\ \alpha_{\lambda_1\lambda_2}^A(\omega)\alpha_{\lambda_3\lambda_4}^B(\omega')V_{\lambda_2\lambda_3}(K)[\bar{\alpha}_{\lambda_4\lambda_6}^A(\omega)\bar{\alpha}_{\lambda_7\lambda_1}^B(\omega')\bar{V}_{\lambda_6\lambda_7}(K) + \bar{\alpha}_{\lambda_5\lambda_4}^A(\omega')\bar{\alpha}_{\lambda_1\lambda_8}^B(\omega)\bar{V}_{\lambda_5\lambda_8}(K')] \end{vmatrix}
$$

$$+ (A \leftrightarrow B) ,$$

(4.1)

where the intermolecular photon propagation tensor is given by the well-known static dipole-dipole interaction tensor of classical electrodynamics,

$$\lim_{KR \to 0} V_{kl}(K,\mathbf{R}) = \frac{1}{4\pi\epsilon_0 R^3}(\delta_{kl} - 3\hat{\mathbf{R}}_k\hat{\mathbf{R}}_l) = V_{kl}^0(K,\mathbf{R}) ,$$

(4.2)

leading to an overall R^{-6} rate dependence. We note in passing that the short-range limit for $V_{kl}(K,\mathbf{R})$ as given by Eq.

(4.2) is traceless; this feature considerably simplifies subsequent results for bimolecular Raman scattering intensities.

2. Free molecules (near zone)

For bimolecular scattering processes where short-range interactions dominate, we find that the rate is

$$I(k') = \left[\frac{\pi C V_I}{13\,500}\right] \rho^A \rho^B V_2 \{(4|e\cdot\bar{e}'|^2 - 1 - |e\cdot e'|^2) \times [-11(A_1 B_1 + A_3 B_3) + 14(A_1 B_3 + A_3 B_1)]$$

$$+ (3|e\cdot\bar{e}'|^2 - 2 + 3|e\cdot e'|^2)[-(A_1 B_2 + A_2 B_1 + A_2 B_3 + A_3 B_2) + 34 A_2 B_2]$$

$$+ 100(-|e\cdot\bar{e}'|^2 + 4 - |e\cdot e'|^2) A_2 B_2$$

$$+ (-|e\cdot\bar{e}'|^2 - 1 + 4|e\cdot e'|^2)[14(A_1 B_1 + A_3 B_3) - 11(A_1 B_3 + A_3 B_1)]\} , \qquad (4.3)$$

where

$$A_1 = \alpha_{\lambda\lambda}^A(k)\bar{\alpha}_{\mu\mu}^A(k) + \alpha_{\lambda\lambda}^A(k)\bar{\alpha}_{\mu\mu}^A(k')$$
$$+ \alpha_{\lambda\lambda}^A(k')\bar{\alpha}_{\mu\mu}^A(k) + \alpha_{\lambda\lambda}^A(k')\bar{\alpha}_{\mu\mu}^A(k') , \qquad (4.4)$$

$$A_2 = \alpha_{\lambda\mu}^A(k)\bar{\alpha}_{\lambda\mu}^A(k) + \alpha_{\lambda\mu}^A(k)\bar{\alpha}_{\lambda\mu}^A(k')$$
$$+ \alpha_{\lambda\mu}^A(k')\bar{\alpha}_{\lambda\mu}^A(k) + \alpha_{\lambda\mu}^A(k')\bar{\alpha}_{\lambda\mu}^A(k') , \qquad (4.5)$$

$$A_3 = \alpha_{\lambda\mu}^A(k)\bar{\alpha}_{\mu\lambda}^A(k) + \alpha_{\lambda\mu}^A(k)\bar{\alpha}_{\mu\lambda}^A(k')$$
$$+ \alpha_{\lambda\mu}^A(k')\bar{\alpha}_{\mu\lambda}^A(k) + \alpha_{\lambda\mu}^A(k')\bar{\alpha}_{\mu\lambda}^A(k') , \qquad (4.6)$$

$$B_1 = \alpha_{vv}^B(k)\bar{\alpha}_{oo}^B(k) + \alpha_{vv}^B(k)\bar{\alpha}_{oo}^B(k')$$
$$+ \alpha_{vv}^B(k')\bar{\alpha}_{oo}^B(k) + \alpha_{vv}^B(k')\bar{\alpha}_{oo}^B(k') , \qquad (4.7)$$

$$B_2 = \alpha_{vo}^B(k)\bar{\alpha}_{vo}^B(k) + \alpha_{vo}^B(k)\bar{\alpha}_{vo}^B(k')$$
$$+ \alpha_{vo}^B(k')\bar{\alpha}_{vo}^B(k) + \alpha_{vo}^B(k')\bar{\alpha}_{vo}^B(k') , \qquad (4.8)$$

$$B_3 = \alpha_{vo}^B(k)\bar{\alpha}_{ov}^B(k) + \alpha_{vo}^B(k)\bar{\alpha}_{ov}^B(k')$$
$$+ \alpha_{vo}^B(k')\bar{\alpha}_{ov}^B(k) + \alpha_{vo}^B(k')\bar{\alpha}_{ov}^B(k') , \qquad (4.9)$$

$$V_2 = \lim_{\substack{c \to 0 \\ U \to \infty}} \int_c^U R^2 dR\, g^{AB}(R)[V_{ij}^0(K,\mathbf{R})\bar{V}_{ij}^0(K',\mathbf{R})$$

$$+ V_{ij}^0(K,\mathbf{R})\bar{V}_{ij}^0(K,\mathbf{R})$$

$$+ V_{ij}^0(K',\mathbf{R})\bar{V}_{ij}^0(K',\mathbf{R})$$

$$+ V_{ij}^0(K',\mathbf{R})\bar{V}_{ij}^0(K,\mathbf{R})] , \qquad (4.10)$$

where, in Eq. (4.10), we emphasize that the near-zone limit of the propagator is taken. Since the principal contribution to the integral occurs in the near zone, the limit of the integral can be extended to infinity without significantly affecting the result. If the irradiation frequency is not close to any absorption band in the fluid, the approximately index-symmetric nature of the scattering tensor leads to the relations $A_2 = A_3$ and $B_2 = B_3$. Further simplification arises in cases where the Raman signal comes from a one-component fluid, where it is apparent that $A_1 = B_1$, $A_2 = B_2$, and $A_3 = B_3$.

B. Far zone

The far-zone limit, defined as the region where $(|K|R, |K'|R) \gg 1$, is normally satisfied when $R > 100$ nm for vibrational scattering processes. Under these condi-

tions the propagator is purely transverse and traceless, taking the form

$$\lim_{\gamma R \to 0} V_{kl}(K,\mathbf{R}) = \frac{1}{4\pi\epsilon_0 R}(\delta_{k\bar{l}}\hat{R}_k\hat{R}_l)\exp(iKR)$$

$$= V_{k\bar{l}}^\infty(K,\mathbf{R}) . \qquad (4.11)$$

In the far zone, it is not possible to ignore the phased terms in the rotational average, and the hence the full expression derived in Sec. III must be used. While the result could be utilized in computational work, it is too complicated in form to allow one to obtain any directly useful information, and will not be further considered here.

Interestingly, the R^{-2} dependence of the intensity equation for a pair of molecules is canceled by the R^2 which arises in the calculation of the scattering intensity for the ensemble, associated with the number of molecules in a shell of a given thickness at distance R. This cancellation leads to a summed result which is independent of the intermolecular distance involved. Of course, this result ignores the finite life of the virtual photon. In any real system, one would have to allow for the possibility that the virtual photon itself is involved in multiple scattering processes.[46] This would lead to the inclusion of a R-dependent radiative damping term giving a result which, to some extent, tails off with R.

C. Bimolecular forward scattering

In what follows we consider the specific case where one of the molecules involved in the cooperative process sits *outside* the interaction volume of the laser beam. In this way it is possible to obtain a simple result, so long as the intensity of light scattered *parallel* to the laser beam is measured. In this forward scattering beam geometry, the intensity of scattered photons created within a cylindrical volume around the collimated beam of the laser has an especially simple form since the interference terms cannot contribute to the scattering intensity. (For cross terms to exist, both molecules involved in the scattering process *must* reside within the interaction volume of the laser.) For this geometry the pair correlation function is defined as

$$g^{AB}(\mathbf{R}_2-\mathbf{R}_1)\rho^A\rho_B$$

$$=\left\langle \sum_{A\in V_{int}}\sum_{B\in(V-V_{int})}\delta(\mathbf{R}_1-\mathbf{R}_A)\delta(\mathbf{R}_2-\mathbf{R}_B)\right\rangle ,$$

$$(4.12)$$

where the sum over A is taken over all molecules within the interaction volume of the laser, the sum over B mole-

cules includes only molecules outside the interaction volume of the laser, and ρ^A,ρ^B are the number densities within these two regions. In order to simplify the problem, we shall assume that this region does not include the near zone. (This is not such a crude approximation since to encroach upon the near zone would require that the detector region be within ~ 100 nm of the interaction volume.) The observed intensity $I_{obs}(\mathbf{k}')$ for this geometry may be written as

$$I_{obs}(\mathbf{k}')=\frac{\pi CV_I}{6750}\rho^A\rho^B V_2\{(4|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2-1-|\mathbf{e}\cdot\mathbf{e}'|^2)[23(\Xi_1\Psi_1+\Xi_3\Psi_3)-2(\Xi_1\Psi_3+\Xi_3\Psi_1)]$$

$$+(3|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2-2+3|\mathbf{e}\cdot\mathbf{e}'|^2)[-7(\Xi_1\Psi_2+\Xi_2\Psi_1+\Xi_2\Psi_3+\Xi_3\Psi_2)+38\Xi_2\Psi_2]$$

$$+100(-|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2+4-|\mathbf{e}\cdot\mathbf{e}'|^2)\Xi_2\Psi_2$$

$$+(-|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2-1+4|\mathbf{e}\cdot\mathbf{e}'|^2)[-2(\Xi_1\Psi_1+\Xi_3\Psi_3)+23(\Xi_1\Psi_3+\Xi_3\Psi_1)]\} ,$$

$$(4.13)$$

where

$$\Xi_1=\alpha^A_{\lambda\lambda}(k)\bar{\alpha}^A_{\mu\mu}(k) , \qquad (4.14)$$

$$\Xi_2=\alpha^A_{\lambda\mu}(k)\bar{\alpha}^A_{\lambda\mu}(k) , \qquad (4.15)$$

$$\Xi_3=\alpha^A_{\lambda\mu}(k)\bar{\alpha}^A_{\mu\lambda}(k) , \qquad (4.16)$$

$$\Psi_1=\alpha^B_{vv}(k')\bar{\alpha}^B_{oo}(k') , \qquad (4.17)$$

$$\Psi_2=\alpha^B_{vo}(k')\bar{\alpha}^B_{vo}(k') , \qquad (4.18)$$

$$\Psi_3=\alpha^B_{vo}(k')\bar{\alpha}^B_{ov}(k') , \qquad (4.19)$$

$$V_2=\int_{V_{det}}d^3R g^{AB}(R)[V^\infty_{ij}(K',\mathbf{R})\bar{V}^\infty_{ij}(K',\mathbf{R})$$

$$+V^\infty_{ij}(K,\mathbf{R})\bar{V}^\infty_{ij}(K,\mathbf{R})] , \qquad (4.20)$$

where V_{det} refers to the volume sampled by the detector. One of the principal advantages of this beam geometry is that it allows one to directly observe the far zone. Another advantage is that the results are of sufficiently simple structure to allow one to interpret the depolarization ratios for any observed Raman band, as will be shown in Sec. VI.

V. PRESSURE DEPENDENCE OF THE BIMOLECULAR SCATTERING RATE

In principle, it is possible to distinguish bands, which are present in the Raman spectrum as a result of bimolecular scattering processes, via their pressure dependence. It is not readily apparent that rates dominated by either long- or short-range energy transfer will exhibit different pressure dependences, but this can be shown as follows.

In the near zone, we find that the intensity of cooperative scattering is extremely sensitive to pressure. This occurs because the pseudostructure of the fluid leads to highly oscillatory behavior close to the origin ($R=0$). In order to obtain an explicit pressure dependence for the intensity in the near zone it is necessary to know something about the density dependence of the pair correlation function for the fluid. Most treatments (see, for example, Ref. 47) expand the pair correlation function in

powers of the density, and following the treatment outlined by Kirkwood,[48,49] the explicit differential pressure dependence may then be written in the form

$$\left|\frac{\partial g(R,\rho,T)}{\partial p}\right|_T=\beta_T\exp[-u(R)/kT]$$

$$\times[\rho g_1(R,T)+2\rho^2 g_2(R,T)+\cdots] ,$$

$$(5.1)$$

where $u(R)$ is the intermolecular potential, β_T is the isothermal compressibility of the fluid defined as[50]

$$\beta_T=-\frac{1}{V_T}\left|\frac{\partial V}{\partial p}\right|_T , \qquad (5.2)$$

and the coefficients $g_n(R,T)$ describe contributions to the correlation function which arise as a result of $(n+2)$-body interactions. The $g_n(R,T)$ are related to the virial coefficients, and are explicitly calculated using the modified cluster integrals of Mayer and Controll.[51]

In the far zone, we find that the $g_n(R,T)$ coefficients in Eq. (5.1) tend to zero, reflecting the fact that the liquid has no long-range structure. In this regime the pair correlation function is stationary with a value close to unity, and the pressure dependence of the scattering intensity should therefore solely reflect the quadratic dependence on density. Writing the intensity equation as

$$I(p)=\phi'\rho^2 , \qquad (5.3)$$

and partially differentiating with respect to pressure at constant temperature, we find that

$$\left|\frac{\partial I(p)}{\partial p}\right|_T=2\phi'\left|\frac{\partial\rho}{\partial p}\right|=2\rho^2\phi'\beta_T=2\beta_T I(p) , \qquad (5.4)$$

so that the differential change in the bimolecular light scattering intensity is simply proportional to the isothermal compressibility.

VI. POLARIZATION DEPENDENCE FOR THE CHROMOPHORE PAIR

The polarization parameters listed in Table I are experimentally variable, their values depending on the scattering angle and the polarization of both the incident and scattered light. In a conventional experiment the scattering angle is usually 90°, and the values for the polarization parameters in several experimental configurations with this beam geometry are listed in Table II.

A. Intramolecular scattering: the chromophore pair

A novel feature of the intramolecular scattering process is the appearance of phase-lag terms arising from scattering interference of the A and B chromophores. It is well known that where the chromophores are dissymmetrically juxtaposed such interference terms result in circular differential scattering.[52,53] Since this property can prove useful in identifying lines in the spectrum attributable to intramolecular scattering, we shall

examine it here in some detail.

The first four columns of Table II give explicit values for the polarization parameters when circularly polarized light is used. The first column labeled $L \rightarrow L$, for example, refers to a scattering geometry where the laser beam is polarized with left-handed helicity, and where the intensity of scattered light with the same helicity is measured; $L \rightarrow R$ refers to a geometry where left-handed circularly polarized light is incident upon the fluid, and where the intensity of scattered light of the opposite handedness is measured. Examination of the columns in Table II reveals that even j value polarization parameters are not changed by reversing the combined helicity of incident and scattered beams, while odd-j valued polarization parameters change sign when the helicity is reversed. Conventionally, this type of chirality is expressed in terms of *circular intensity differentials*. These can be obtained from the leading j_1/j_0 terms in the rate expressions, and are explicitly given by

$$\frac{I(L \rightarrow \|) - I(R \rightarrow \|)}{I(L \rightarrow \|) + I(R \rightarrow \|)} = \frac{(\omega' - \omega)RT^{(1;2)}}{cT^{(0;2)}} ,$$ (6.1)

$$\frac{I(L \rightarrow \perp) - I(R \rightarrow \perp)}{I(L \rightarrow \perp) + I(R \rightarrow \perp)} = \frac{(\omega' - \omega)R(T^{(1;1)} + T^{(1;3)} + T^{(1;4)} - T^{(1;6)})}{c(T^{(0;1)} + 2T^{(0;0)} + T^{(0;3)})} .$$ (6.2)

The coefficient given expression in Eq. (6.1) is that most commonly measured. This has the simplest structure of all, being finite so long as the molecular response tensor $T^{(1;2)}$ is not zero, which is generally the case so long as the Raman polarizability tensor for the transition is not isotropic. The second differential scattering coefficient is included for completeness. The most interesting feature of these dissymmetry factors is their linear dependence upon the intrachromophore distance R. This behavior has been noticed in connection with circular differential Rayleigh and Raman scattering and optical rotation.[54]

In addition to the two polarization ratios above, it is possible to define a third ratio, which measures the degree of helicity reversal; this has the explicit form

$$\frac{I(L \rightarrow L) - I(L \rightarrow R)}{(L \rightarrow L) + I(L \rightarrow R)} = \frac{2(\omega' - \omega)R(-2T^{(1;1)} + T^{(1;2)} + 2T^{(1;5)} + T^{(1;6)})}{c(T^{(0;1)} + 4T^{(0;2)} + T^{(0;3)})} .$$ (6.3)

TABLE II. Values of the polarization parameters $A^{(j;p)}$ for 90° scattering experiments for eight different polarization geometries.

j	p	$L \rightarrow L$	$R \rightarrow R$	$L \rightarrow R$	$R \rightarrow L$	$L \rightarrow \perp$	$R \rightarrow \perp$	$L \rightarrow \|$	$R \rightarrow \|$
0	1	1/4	1/4	1/4	1/4	1/2	1/2	0	0
0	2	1	1	1	1	1	1	1	1
0	3	1/4	1/4	1/4	1/4	1/2	1/2	0	0
1	1	0	0	$i/2$	$-i/2$	$i/2$	$-i/2$	0	0
1	2	$-i/2$	$i/2$	$i/2$	$-i/2$	i	$-i$	i	$-i$
1	3	$i/2$	$-i/2$	0	0	$i/2$	$-i/2$	0	0
1	4	$i/2$	$-i/2$	0	0	$i/2$	$-i/2$	0	0
1	5	$i/2$	$-i/2$	$-i/2$	$i/2$	0	0	0	0
1	6	0	0	$-i/2$	$i/2$	$-i/2$	$i/2$	0	0
2	1	1/6	1/6	$-1/3$	$-1/3$	$-1/6$	$-1/6$	0	0
2	2	1/6	1/6	1/6	1/6	$-1/3$	$-1/3$	2/3	2/3
2	3	$-1/3$	$-1/3$	1/6	1/6	$-1/6$	$-1/6$	0	0
2	4	$-1/3$	$-1/3$	1/6	1/6	$-1/6$	$-1/6$	0	0
2	5	1/6	1/6	$-1/3$	$-1/3$	1/6	1/6	1/6	1/6
2	6	1/6	1/6	$-1/3$	$-1/3$	$-1/6$	$-1/6$	0	0
3	1	$i/10$	$-i/10$	$i/10$	$-i/10$	$-i/5$	$i/5$	$2i/5$	$-2i/5$
3	2	$2i/5$	$-2i/5$	0	0	$i/10$	$-i/10$	$-3i/10$	$3i/10$
3	3	0	0	$2i/5$	$-2i/5$	$i/10$	$-i/10$	$3i/10$	$-3i/10$
4	1	3/20	3/20	3/20	3/20	1/70	1/70	11/35	11/35

This coefficient is of interest since its value for *right-angled scattering* is only nonzero if the chemical species responsible for the scattering is chiral. This remark applies both to normal Raman scattering by individual free molecules, and to cooperative scattering by chromophore pairs. In the latter case the chirality refers to the coupled system, and analysis of the detailed structure of the numerator of the terms in Eq. (6.3) reveals that the condition is only satisfied where the chromophores are dissymmetrically placed with respect to each other, and where their Raman polarizability tensors are anisotropic. This situation corresponds exactly to the well-known coupled-oscillator model for chiral behavior.[55] For *forward* scattering, the reversal ratio can be nonzero even for achiral systems; it then represents a measure of the degree to which the handedness of the laser beam dresses the molecular states of the free molecules and thereby induces a chirality.[56,57]

B. Free molecules

Circular differential scattering from free molecules can only be manifest by chiral species, where the effect results from interference between electric dipole and either magnetic dipole or electric quadrupole interactions.[48] To the level of approximation considered here, bimolecular scattering *per se* does not contribute to differential scattering in an isotropic fluid, as all odd-order Bessel function terms vanish when the further necessary orientational averages are effected. However, it is possible to glean some useful properties of the bimolecular scattering path via polarization characteristics of the radiation field. These polarization experiments are best conducted for the specific forward scattering geometry discussed earlier, where the detector measures the intensity of the light scattered *outside* the interaction volume of the laser, but parallel to the laser beam. Under these conditions one is studying the far-zone properties. If the beam is not close to any one-photon absorption bands, we find that the observed scattering intensity equation (4.13) for a single component fluid reduces to

$$I_{\text{obs}}(\mathbf{k}') = \frac{\pi C V_I}{6750} \rho^A \rho^B V_2 \{ (4|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 - 1 - |\mathbf{e}\cdot\mathbf{e}'|^2)[23(\Xi_1^2 + \Xi_3^2) - 4\Xi_1\Xi_3]$$

$$+ (3|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 - 2 + 3|\mathbf{e}\cdot\mathbf{e}'|^2)[-14(\Xi_1\Xi_2 + \Xi_2\Xi_3) + 38\Xi_2^2]$$

$$+ 100(-|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 + 4 - |\mathbf{e}\cdot\mathbf{e}'|^2)\Xi_2^2$$

$$+ (-|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2 - 1 + 4|\mathbf{e}\cdot\bar{\mathbf{e}}'|^2)[-2(\Xi_1^2 + \Xi_3^2) + 46\Xi_1\Xi_3] \} . \tag{6.4}$$

The first notable aspect of Eq. (6.4) is that the depolarization ratio becomes

$$\frac{I(\perp \rightarrow \|)}{I(\perp \rightarrow \perp)} = \frac{-21\Xi_1^2 + 331\Xi_2^2 - 14\Xi_1\Xi_2}{42\Xi_1^2 + 342\Xi_2^2 + 32\Xi_1\Xi_2} \tag{6.5}$$

for transitions that occur purely as a result of the bimolecular scattering mechanism. Here $I(\perp \rightarrow \perp)$ refers to the rate of forward scattering of light with the same polarization as the incident beam; $I(\perp \rightarrow \|)$ refers to the rate at which light of polarization perpendicular to the incident beam is emitted. In order to glean useful symmetry properties from the depolarization ratio, it is convenient to cast the molecular invariants in irreducible

tensor form. For index-symmetric polarization tensors we find that the two molecular tensor invariants may be written as

$$\Xi_1 = \alpha_{\lambda\lambda}\alpha_{\mu\mu} = 3\alpha_{\lambda\mu}^{(0+)}\alpha_{\lambda\mu}^{(0+)} , \tag{6.6}$$

$$\Xi_2 = \alpha_{\lambda\mu}\alpha_{\lambda\mu} = \alpha_{\lambda\mu}^{(2+)}\alpha_{\lambda\mu}^{(2+)} + \alpha_{\lambda\mu}^{(0+)}\alpha_{\lambda\mu}^{(0+)} , \tag{6.7}$$

where the superscripted $(n+)$ refers to a tensor of weight n and even parity. Tensors of weight $(0+)$ are isomorphic with the totally symmetric representation of the molecular point group, while the tensors of weight $(2+)$ transform as traceless rank-two tensors of even parity. Casting Eq. (6.5) into an irreducible tensor format gives the result

$$\frac{I(\perp \rightarrow \|)}{I(\perp \rightarrow \perp)} = \rho(\perp) = \frac{100\alpha_{\lambda\mu}^{(0+)}\alpha_{\lambda\mu}^{(0+)}\alpha_{vo}^{(0+)}\alpha_{vo}^{(0+)} + 620\alpha_{\lambda\mu}^{(0+)}\alpha_{\lambda\mu}^{(0+)}\alpha_{vo}^{(2+)}\alpha_{vo}^{(2+)} + 331\alpha_{\lambda\mu}^{(2+)}\alpha_{\lambda\mu}^{(2+)}\alpha_{vo}^{(2+)}\alpha_{vo}^{(2+)}}{816\alpha_{\lambda\mu}^{(0+)}\alpha_{\lambda\mu}^{(0+)}\alpha_{vo}^{(0+)}\alpha_{vo}^{(0+)} + 780\alpha_{\lambda\mu}^{(0+)}\alpha_{\lambda\mu}^{(0+)}\alpha_{vo}^{(2+)}\alpha_{vo}^{(2+)} + 342\alpha_{\lambda\mu}^{(2+)}\alpha_{\lambda\mu}^{(2+)}\alpha_{vo}^{(2+)}\alpha_{vo}^{(2+)}} . \tag{6.8}$$

Thus the depolarization ratio $\rho(\perp)$ has the value $\frac{25}{204}$ for a pure weight-zero transition and $\frac{331}{342}$ for a pure weight-two transition. It is interesting to note that the depolarization ratios obtained for transitions that occur solely as a result of cooperative scattering are thus slightly higher than those obtained in the dilute gas approximation; hence we would expect that in condensed phases multibody scattering mechanisms would lead to increases in the observed Raman depolarization ratios.

VII. CONCLUSION

To conclude, in this paper a quantum electrodynamical theory of cooperative scattering in fluids has been developed. Using the retarded multipolar expansion of Power, Zienau, and Woolley fully causal intensity equations for bimolecular scattering, which are valid over all intermolecular separations, have been derived. For processes involving cooperative scattering between free mol-

ecules, equations have been given for the observed scattering intensity which take full account of the molecular distribution of the liquid. It has been shown how these results can be employed to elucidate the pressure dependence of the process, and how, for a specific beam geometry, it is possible to define a depolarization ratio which can be used to verify the symmetry of the two transitions. In the case where the molecules involved in the bimolecular scattering process are held in fixed orientation with respect to one another, it has been illustrated how the manifestation of a differential scattering effect may be used in identifying these bands in the spectrum. In assessing the importance of the effects described, it may be noted that short-range cooperative Raman effects are typically smaller than their single-center counterparts by a factor of the order of $\alpha/\epsilon_0 R^3$, where α/ϵ_0 is the Raman polarizability volume. For an intermolecular separation on the angstrom scale, this factor can be expected to be of the order of 0.1–0.01. Exploitation of resonance conditions may, however, substantially offset the intensity diminution associated with this factor. It should therefore be possible using the methods described above, along with modern Fourier transform Raman spectrometers, to identify such cooperative contributions.

APPENDIX: PROOF THAT COOPERATIVE RAMAN SCATTERING IS INCOHERENT

In the result obtained in Sec. II of this paper, it is illustrated how the Fermi rule result may be obtained, and in particular how the intensity of cooperatively scattered light is proportional to the square of the matrix element M_{fi}. For an ensemble the latter may be written as

$$M_{fi} = \sum_{A,B\neq A} e^{-i(\mathbf{k}'\cdot\mathbf{R}_b - \mathbf{k}\cdot\mathbf{R}_a)} \alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times(-\nabla^2\delta_{jk}+\nabla_j\nabla_k)\frac{e^{i\mathbf{K}\cdot(\mathbf{R}_B-\mathbf{R}_A)}}{R}, \qquad (A1)$$

where the summation is over all molecules in the ensemble, and all other terms have their usual meanings. Taking the modulus square of Eq. (A1), we find that there are two types of contribution,

$$|M_{fi}|^2 = \sum_{A,B\neq A} e^{-i(\mathbf{k}'\cdot\mathbf{R}_B - \mathbf{k}\cdot\mathbf{R}_A)} \sum_{C,D\neq C} e^{i(\mathbf{k}'\cdot\mathbf{R}_D - \mathbf{k}\cdot\mathbf{R}_C)} \alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times(-\nabla^2\delta_{jk}+\nabla_j\nabla_k)\frac{e^{i\mathbf{K}\cdot(\mathbf{R}_B-\mathbf{R}_A)}}{(R_B-R_A)}\bar{\alpha}_{mn}^C(k)\bar{\alpha}_{op}^D(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')$$

$$\times(-\nabla^2\delta_{no}+\nabla_n\nabla_o)\frac{e^{-i\mathbf{K}\cdot(\mathbf{R}_D-\mathbf{R}_C)}}{(R_D-R_C)}. \qquad (A2)$$

These contributions are (i) the *coherent* contribution, which arises when $A\neq C,D$ and $B\neq C,D$; and (ii) the *incoherent* contribution, which arises when $A=C$ and $B=D$. Since it is the purpose of this appendix to show that the coherent part does not contribute to the scattering intensity, we shall specifically concentrate upon this term in Eq. (A2).

In order to arrive at the proof we shall consider the coherent contribution that arises from two arbitrary points within the liquid, specifically $\mathbf{R}_1$ and $\mathbf{R}_3$. These points correspond to the sites where the cooperative scattering is initiated, i.e.,the points where the laser photons are annihilated. Thus

$$|M_{fi}|^2(R_1,R_3) = \sum_{\substack{A,B\neq A \\ C\neq A, D\neq C}} \delta(\mathbf{R}_1-\mathbf{R}_A)\delta(\mathbf{R}_3-\mathbf{R}_C)e^{-i(\mathbf{k}'\cdot\mathbf{R}_B - \mathbf{k}\cdot\mathbf{R}_1) + i(\mathbf{k}'\cdot\mathbf{R}_D - \mathbf{k}\cdot\mathbf{R}_3)}$$

$$\times\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')(-\nabla^2\delta_{jk}+\nabla_j\nabla_k)\frac{e^{i\mathbf{K}\cdot(\mathbf{R}_B-\mathbf{R}_1)}}{(R_B-R_1)}$$

$$\times\bar{\alpha}_{mn}^C(k)\bar{\alpha}_{op}^D(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')(-\nabla^2\delta_{no}+\nabla_n\nabla_o)\frac{e^{-i\mathbf{K}\cdot(\mathbf{R}_D-\mathbf{R}_3)}}{(R_D-R_3)}. \qquad (A3)$$

Using the methods of Sec. III we can write this equation as

$$|M_{fi}|^2(R_1,R_3) = \int_{-\infty}^{\infty}d^3R_2\int_{-\infty}^{\infty}d^3R_4\rho(\mathbf{R}_2-\mathbf{R}_1)\rho(\mathbf{R}_4-\mathbf{R}_3)e^{-i(\mathbf{k}'\cdot\mathbf{R}_2 - \mathbf{k}\cdot\mathbf{R}_1) + i(\mathbf{k}'\cdot\mathbf{R}_4 - \mathbf{k}\cdot\mathbf{R}_3)}$$

$$\times\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')(-\nabla^2\delta_{jk}+\nabla_j\nabla_k)\frac{e^{i\mathbf{K}\cdot(\mathbf{R}_2-\mathbf{R}_1)}}{(R_2-R_1)}$$

$$\times\bar{\alpha}_{mn}^C(k)\bar{\alpha}_{op}^D(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')(-\nabla^2\delta_{no}+\nabla_n\nabla_o)\frac{e^{-i\mathbf{K}\cdot(\mathbf{R}_4-\mathbf{R}_3)}}{(R_4-R_3)}. \qquad (A4)$$

Now consider the integral over $\mathbf{R}_2$,

$$\int_{-\infty}^{\infty} d^3\mathbf{R}_2\rho(\mathbf{R}_2-\mathbf{R}_1)e^{i\mathbf{k}'\cdot\mathbf{R}_2}(-\nabla^2\delta_{jk}+\nabla_j\nabla_k)\frac{e^{i\mathbf{K}\cdot(\mathbf{R}_2-\mathbf{R}_1)}}{(R_2-R_1)}=\int_{-\infty}^{\infty} d^3\mathbf{R}_2\Lambda_{jk}(\mathbf{R}_2-\mathbf{R}_1)e^{i\mathbf{k}'\cdot\mathbf{R}_2}\ , \tag{A5}$$

where $\Lambda_{jk}(\mathbf{R}_2-\mathbf{R}_1)$ is the Fourier transform, i.e.,

$$\Lambda_{jk}(\mathbf{R}_2-\mathbf{R}_1)=(2\pi)^{-3}\int_{-\infty}^{\infty} d^3\mathbf{q}\Lambda_{jk}(\mathbf{q})e^{i\mathbf{q}\cdot(\mathbf{R}_2-\mathbf{R}_1)}\ . \tag{A6}$$

Substituting this result into Eq. (A5) we obtain the result

$$\int_{-\infty}^{\infty} d^3\mathbf{R}_2\Lambda_{jk}(\mathbf{R}_2-\mathbf{R}_1)e^{i\mathbf{k}'\cdot\mathbf{R}_2}=\frac{1}{8\pi^3}\int_{-\infty}^{\infty} d^3\mathbf{q}\Lambda_{jk}(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}_1}\int_{-\infty}^{\infty} d^3\mathbf{R}_2e^{i(\mathbf{k}'+\mathbf{q})\cdot\mathbf{R}_2}$$

$$=\frac{1}{8\pi^3}\int_{-\infty}^{\infty} d^3\mathbf{q}\Lambda_{jk}(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}_1}\delta(\mathbf{k}'+\mathbf{q})$$

$$=\frac{1}{8\pi^3}\Lambda_{jk}(-\mathbf{k}')e^{i\mathbf{k}'\cdot\mathbf{R}_1}\ . \tag{A7}$$

Naturally a similar result is obtained for the second integral in Eq. (A4); substituting this result and its counterpart into (A4) gives

$$|M_{fi}|^2(\mathbf{R}_1,\mathbf{R}_3)=\alpha_{ij}^A(k)\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')\bar{\alpha}_{mn}^C(k)$$

$$\times\bar{\alpha}_{op}^D(k')\bar{e}_m(\mathbf{k})e_p(\mathbf{k}')\frac{1}{4\pi^2}$$

$$\times\Lambda_{jk}(-\mathbf{k}')\Lambda_{no}(\mathbf{k}')$$

$$\times e^{-i(\mathbf{k}'-\mathbf{k})\cdot(\mathbf{R}_3-\mathbf{R}_1)} \tag{A8}$$

In order to obtain the matrix element for the ensemble it is necessary to sum over all points within the fluid. If we convert the sum to an integral over $\mathbf{R}_1$ and $\mathbf{R}_3$, we find that Eq. (A8) is only nonzero when $\mathbf{k}'-\mathbf{k}=0$ (since the exponential gives a δ function), completing the proof.

As a final aside it is worth considering the interference terms that arise in the incoherent contribution, since it is by no means apparent that these terms in Eq. (A2) will survive when one performs the distributional average. For these terms the squaring of the matrix element gives terms of the type

$$|M_{fi}|^2(\mathbf{R}_1)=\sum_{A,B\neq A}\delta(\mathbf{R}_1-\mathbf{R}_A)e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_B-\mathbf{R}_1)}$$

$$\times\bar{\alpha}_{mn}^A(k')\bar{\alpha}_{op}^B(k)e_p(\mathbf{k}')\bar{e}_m(\mathbf{k})\alpha_{ij}^A(k)$$

$$\times\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times V_{jk}(K,\mathbf{R}_2-\mathbf{R}_1)\bar{V}_{no}(K',\mathbf{R}_2-\mathbf{R}_1)\ ,$$

which give, on performing the distributional average,

$$|M_{fi}|^2(\mathbf{R}_1)=\int_{-\infty}^{\infty} d^3\mathbf{R}_2\rho(\mathbf{R}_2-\mathbf{R}_1)e^{i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}_2-\mathbf{R}_1)}$$

$$\times\bar{\alpha}_{mn}^A(k')\bar{\alpha}_{op}^B(k)e_p(\mathbf{k}')\bar{e}_m(\mathbf{k})\alpha_{ij}^A(k)$$

$$\times\alpha_{kl}^B(k')e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times V_{jk}(K,\mathbf{R}_2-\mathbf{R}_1)\bar{V}_{no}(K',\mathbf{R}_2-\mathbf{R}_1)\ .$$

Restricting our attention to the integral over $\mathbf{R}_2$,

$$\int_{-\infty}^{\infty} d^3\mathbf{R}_2\rho(\mathbf{R}_2-\mathbf{R}_1)V_{jk}(K,\mathbf{R}_2-\mathbf{R}_1)$$

$$\times V_{no}(K',\mathbf{R}_2-\mathbf{R}_1)e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_2}$$

$$=\int_{-\infty}^{\infty} d^3\mathbf{R}_2\Lambda_{jkno}(\mathbf{R}_2-\mathbf{R}_1)e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_2}\ ,$$

where we have defined the Fourier transform

$$\Lambda_{jkno}(\mathbf{R}_2-\mathbf{R}_1)=(2\pi)^{-3}\int_{-\infty}^{\infty} d^3\mathbf{q}\Lambda_{jkno}(\mathbf{q})e^{i(\mathbf{R}_2-\mathbf{R}_1)\cdot\mathbf{q}}$$

which allows to express the modulus square of the defined matrix element as

$$|M_{fi}|^2=\alpha_{ij}^A(k)\alpha_{kl}^B(k')\bar{\alpha}_{mn}^A(k')\bar{\alpha}_{op}^B(k)e_i(\mathbf{k})\bar{e}_l(\mathbf{k}')$$

$$\times e_n(\mathbf{k}')\bar{e}_o(\mathbf{k})\frac{1}{8\pi^3}\Lambda_{jkno}(\mathbf{k}-\mathbf{k})\ ,$$

which is simply the result obtained by convolution of the original integral over $\mathbf{R}$.

[1]D. Frenkel and J. P. McTague, J. Chem. Phys. **72**, 2801 (1980).
[2]T. Bancewicz and S. Kielich, J. Chem. Phys. **75**, 107 (1981).
[3]P. A. Madden and D. Tildesley, Mol. Phys. **55**, 969 (1985).
[4]T. W. Zerda, X. Song, J. Jonas, B. M. Landanyi, and L. C. Gerger, J. Chem. Phys. **87**, 870 (1987).
[5]R. P. Hobza and R. Zahradnik, *Weak Intermolecular Interactions in Chemistry and Biology* (Elsevier, New York, 1980), p. 24.
[6]S. Gburski, J. Samios, and Th. Dorfmüller, J. Chem. Phys. **86**,

383 (1987).
[7]J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).
[8]D. P. Craig and T. Thirunamachandran, Phys. Rev. A **28**, 2663 (1983).
[9]S. P. Keating, Mol. Phys. **48**, 655 (1983).
[10]A. Sokolowska, J. Raman Spectrosc. **18**, 513 (1987).
[11]S. Brates and G. Tarjus, in *Raman Spectroscopy, Linear and Nonlinear*, edited by J. Lascombe and P. V. Huong,

(Springer-Verlag, New York, 1979), p. 313.

[12]H. W. Schrötter and H. W. Klockner, in *Raman Spectroscopy of Gases and Liquids,* edited by A. Weber (Springer-Verlag, Berlin 1979), pp. 123–166.

[13]A. Garbi and Y. L. Duff, Physica A**90**, 177 (1976).

[14]E. A. Power and S. Zienau, Philos. Trans. R. Soc. London Ser. A **251**, 427 (1959).

[15]M. Babiker, E. A. Power, and T. Thirunamachandran, Proc. R. Soc. London Ser. A **338**, 238 (1974).

[16]D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Academic, New York, 1984), pp. 62, 63.

[17]E. A. Power and T. Thirunamachandran, Am. J. Phys. **46**, 370 (1978).

[18]M. Göppert-Mayer, Ann. Phys. (Leipzig) **9**, 273 (1931).

[19]P. I. Richards, Phys. Rev. **73**, 254 (1948).

[20]M. O. Scully, Proc. Int. Sch. Phys. "Enrico Fermi" XLII, 586 (1969).

[21]R. G. Woolley, Proc. R. Soc. London Ser. A **321**, 557 (1971).

[22]R. G. Woolley, Mol. Phys. **22**, 1013 (1971).

[23]J. Savolainen and S. Stenholm, Am. J. Phys. **40**, 667 (1972).

[24]Z. Fried, Phys. Rev. A **8**, 2835 (1973).

[25]R. G. Woolley, Adv. Chem. Phys. **23**, 153 (1975).

[26]P. W. Langhoff, S. T. Epstein, and M. Karplus, Rev. Mod. Phys. **44**, 602 (1974).

[27]A. Ganguly and J. L. Birman, Phys. Rev. **162**, 806 (1967).

[28]D. P. Craig and T. Thirunamachandran, Ref. 16, p. 273.

[29]E. Fermi, *Nuclear Physics* (University of Chicago Press, Chicago, 1950).

[30]R. V. Churchill, J. W. Brown and R. F. Verhey, *Complex Variables and Applications,* 3rd ed. (McGraw-Hill International, London, 1974), p. 182.

[31]P. W. Atkins, *Molecular Quantum Mechanics,* 2nd ed. (Oxford University Press, New York, 1983), p. 198.

[32]E. A. Power, *Introductory Quantum Electrodynamics* (Longmans, London, 1964), Chap. 7.

[33]W. P. Healy, *Non-Relativistic Quantum Electrodynamics* (Academic, New York, 1982), p. 133.

[34]R. Loudon, *The Quantum Theory of Light* (Oxford University Press, Oxford, 1973), p. 53.

[35]R. P. Feynman, *Quantum Electrodynamics* (Benjamin/Cummings, New York, 1962), p. 85.

[36]D. L. Andrews and B. S. Sherborne, J. Chem. Phys. **86**, 4011 (1987).

[37]R. Loudon, Proc. R. Soc. London Ser. A **275**, 218 (1963).

[38]R. S. Knox, *Advances in Solid State Physics,* Suppl. 5 of *Theory of Excitons,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1950), p. 2.

[39]R. M. Martin and L. Falicov, *Light Scattering in Solids,* edited by M. Cardona (Springer, New York, 1975), Chap. 3.

[40]D. L. Andrews and T. Thirunamachandran, J. Chem. Phys. **67**, 5026 (1977).

[41]D. L. Andrews and M. J. Harlow, Phys. Rev. A **29**, 2796 (1983).

[42]D. L. Andrews and N. P. Blake, J. Phys. A **22**, 49 (1989).

[43]D. L. Andrews and W. A. Ghoul, Phys. Rev. A **25**, 2647 (1982).

[44]V. V. Mikhailov, J. Phys. A **10**, 147 (1977).

[45]D. L. Andrews and M. J. Harlow, J. Chem. Phys. **80**, 4753 (1984).

[46]D. L. Andrews and K. P. Hopkins, J. Chem. Phys. **89**, 4461 (1988).

[47]C. H. Wang, *Spectroscopy of Condensed Media—Dynamics of Molecular Interactions* (Academic, New York, 1985), p. 58.

[48]D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, Oxford, 1987), p. 201.

[49]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 209.

[50]W. H. Flygare, *Molecular Structure and Dynamics* (Prentice-Hall, New York, 1978), p. 525.

[51]J. E. Mayer and E. Montroll, J. Chem. Phys. **9**, 2 (1941).

[52]L. D. Barron and A. D. Buckingham, J. Am. Chem. Soc. **96**, 4769 (1974).

[53]D. L. Andrews and T. Thirunamachandran, Proc. R. Soc. London Ser. A **358**, 311 (1977).

[54]L. D. Barron, J. Chem. Soc. Faraday Trans. 2 **71**, 293 (1975).

[55]L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, 1972).

[56]J. P. Riehl and F. S. Richardson, Chem. Phys. Lett. **42**, 501 (1976).

[57]R. Clark, S. R. Jeyes, A. J. McCaffery, and R. J. Shatwell, J. Am. Chem. Soc. **96**, 5586 (1974).